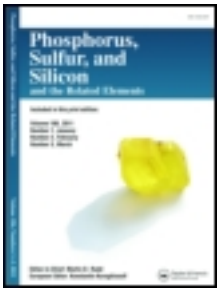

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Antimony (III) Sulfate Catalyzed One-Pot Synthesis of 2,3-Disubstitutedindoles

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Antimony (III) Sulfate Catalyzed One-Pot Synthesis of 2,3-Disubstitutedindoles

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A novel one-pot Fischer indole synthesis approach has been developed by using antimony (III) sulfate as the catalyst. Good yields were obtained after reacting phenylhydrazines hydrochlorides and ketones in refluxing methanol. The exclusive formation of 2,3- disubstituted indoles was observed in the reaction of ethyl methyl ketone with phenylhydrazines. One-pot synthesis of indole-3-propanol using dihydropyran has also been described. The use of reusable antimony (III) sulfate as a catalyst makes this method both economically and environmentally friendly.

Keywords Antimony (III) sulfate; cyclohexanone; Fischer indole synthesis; one pot; phenylhydrazine hydrochlorides

INTRODUCTION

Indoles are probably the most widely distributed heterocyclic compounds in nature. Tryptophan-derived substances in the plant kingdom include indole-3-yl-acetic acid, a plant growth regulator harmone, and a huge number and structural variety of secondary metabolites are the indole alkaloids.[1] Although many methods have been developed for the synthesis of indoles,[2] Fischer indole synthesis is still one of the most versatile and widely employed methodologies for the preparation of indoles and related biologically active indole derivatives.[3] The Fischer

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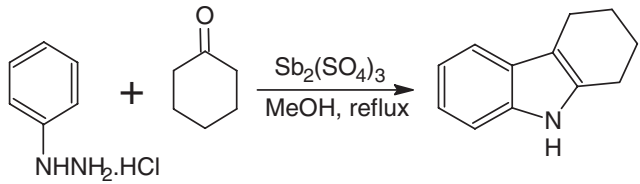
indole synthesis involves the acid or Lewis acid catalyzed rearrangement of aryl hydrazone with elimination of ammonia via [3, 3] sigma tropic rearrangement.[4] Various catalysts have been used to achieve the cyclization of aryl hydrazones derived from ketones, including Bronsted acids (H_2SO_4, HCl, PPA, AcOH).[5] Lewis acids ($ZnCl_2$, $TiCl_4$, PCl_5)[6] and solid acids (zeolite, montmorillonite clay)[7] have been reported for the synthesis of the indole nucleus. However, search for a new catalyst is still being actively pursued, because the existing methods suffer from at least one drawback. Reported Bronsted and Lewis acids are not ecofriendly, they are hazardous or difficult to reuse, and they are used either in equimolar quantity or in large excess. PPA is used in eight- to ninefold excess by weight, whereas $ZnCl_2$ is used in threefold excess. Although utilization of solid acids may solve the above problems, solid acids have their own shortcomings, which limit their application to some degree, such as restricted accessibility of the matrix bound acidic sites, rapid deactivation, and decrease of active site per area. Noncatalytic Fischer indole synthesis has also been studied in different solvents, such as ethylene glycol, diethyl glycol, and tetralin. However high temperatures above 200°C are required for such cyclization.[8]

The development of a one-pot approach to the Fischer indole synthesis is attractive mostly because of its significance from both commercial and ecological point of view. In these methods, ketones and phenylhydrazines are reacted in the presence of an acid catalyst, resulting in the formation of hydrazone and subsequent [3 + 3] sigma tropic rearrangement, which results in the formation of the indoles. This one-pot procedure obviates the preparation or isolation of the unstable aryl hydrazone. Recently there are reports concerning one-pot Fischer indole synthesis using Lewis acid ionic liquids such as 1-butyl-pyridinium chloride.$3AlCl_3$ or choline chloride.$2ZnCl_2$, respectively.[9] In spite of diverse synthetic approaches developed so far for the indole synthesis, there is still a need for the development of an environmentally and economically friendly catalyst. We thought that one-pot Fisher indole synthesis promoted by an environmentally friendly catalyst seems to address this issue. This can be achieved by the use of insoluble soft Lewis acid that is stable to water and alcohols. Recently, we have described the synthetic utility of $Sb_2(SO_4)_3$ as a catalyst in the synthesis of bis-indoles.[10] The $Sb_2(SO_4)_3$ acid is an inexpensive, stable solid, and it is easily available. $Sb_2(SO_4)_3$is easier to handle than halides, such as $ZnCl_2$, $TiCl_4$, PCl_5, and protic acids such as PPAand HCl. In this communication, we report the synthesis of 2,3-disustituted indoles via one-pot Fischer indole reaction using $Sb_2(SO_4)_3$ as a reusable catalyst. So far, to the best of our knowledge, $Sb_2(SO_4)_3$ has not been used in Fischer indole synthesis.



1a **2a** **3a**

SCHEME 1 Screening of the reaction conditions for the synthesis of **3a**.

RESULTS AND DISCUSSION

To begin laying the foundation for exploring the catalytic activity of $Sb_2(SO_4)_3$ in one-pot Fischer indole synthesis, we chose phenylhydrazine hydrochloride **1a** and cyclohexanone **2a**. When the mixture of phenylhydrazine hydrochloride and cyclohexanone was refluxed for 30 min in MeOH in the presence of a catalytic amount of antimony (III) sulfate (Scheme 1), tetrahydrocarbazole was formed. Encouraged by this result, we undertook the detailed study of this reaction. Thus initially, the one-pot reaction of phenylhydrazine hydrochloride with cyclohexanone was carried out as a model reaction in various solvents to investigate the solvent effect. The results are summarized in Table I. Methanol, ethanol, and acetonitrile were found to be better solvents for this transformation. However, the best results were achieved by carrying out the reaction in MeOH at reflux temperature afforded tetrahydrocarbazoles

TABLE I Effect of Solvents in the Synthesis of Tetrahydrocarbazoles[a]

Entry	Solvent	$Sb_2(SO_4)_3$(mol%)	Time (min)	Yields (%)[b]
1	MeOH	5	90	80
2	MeOH	10	40	95
3	MeOH	15	40	91
4	EtOH	10	55	92
5	CH_3CN	10	65	82
6	THF	10	70	60
7	CH_2Cl_2	10	240	48
8	EtOAc	10	125	52
9	Toluene	10	75	55
10	MeOH	10	40	95, 88, 85
11	MeOH	0	240	15

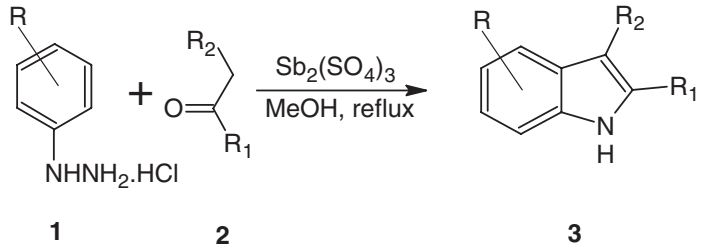
[a]All reactions were carried out at reflux temperature.
[b]Isolated yields.

in 95% yield, respectively. Furthermore, we set out to establish the optimal amount of $Sb_2(SO_4)_3$; the reaction with a 5mol% catalyst loading gave a 80% yield after 90 min (entry 1), whereas the best result (95%) was obtained with 10mol% $Sb_2(SO_4)_3$ (entry 2) after 40 min. Furthermore, when the reaction was carried out in absence of $Sb_2(SO_4)_3$, formation of tetrahydrocarbazoles was less (15%) after 240 minutes (entry 11). Another advantage of the use of $Sb_2(SO_4)_3$ was that it could be easily recovered and recycled in subsequent reactions without significant decrease in the catalytic activity. $Sb_2(SO_4)_3$ was easily separated from the reaction mixture by simple extraction and filtration. The catalyst could be recycled three times with out obvious loss of activity (entry 10: 95%, 1st run; 88%, 2nd run; 85% 3rd run.).

In order to study the generality of this process, it was decided to react a wide variety of functionalized phenylhydrazine hydrochlorides with different ketones (Scheme 2). The results are summarized in Table II. These results demonstrate that this one-pot indole synthesis is quite general and can accept a wide variety of substitution both on phenyl hydrazine backbone as well as carbonyl component.

An important issue of the Fischer indole synthesis in the cyclization of the phenyl hydrazones derived from unsymmetrical ketones is that the direction of cyclization is governed by the acidity of the reaction medium.[11] The lower acid concentration or weaker acid promote cyclization towards the more branched carbon, and higher acid concentrations or stronger acid enhance the extent of cyclization at the less branched positions. As $Sb_2(SO_4)_3$ provides a weaker acid system, direction of cyclization occurred to produce more branched carbon during indole synthesis.

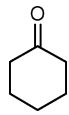
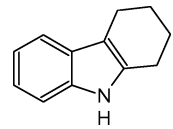
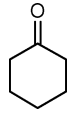
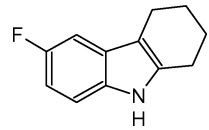
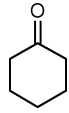
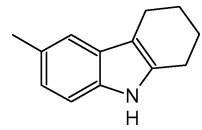
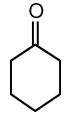
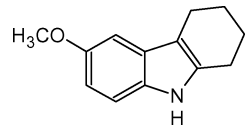
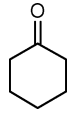
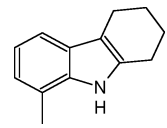
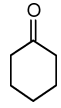
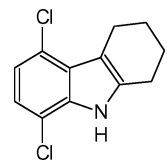
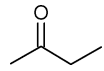
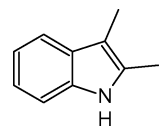
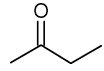
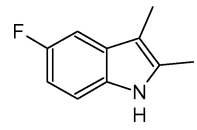
Recently Kevin et al. reported the one-pot synthesis of indoles from cyclic enol ethers in H_2SO_4 and acetonitrile/N,N-dimethylacetamide as cosolvent. Anticipating similar results, we tried one-pot synthesis of indole-3-propanol derivatives **4** by using



1 **2** **3**

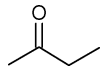
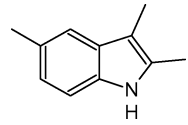
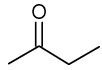
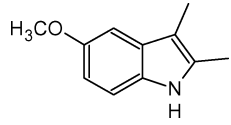
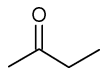
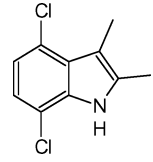
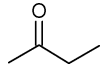
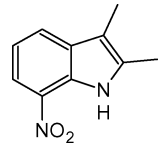
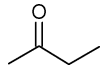
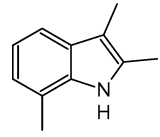
SCHEME 2 Synthesis of 2,3-disubstituded indoles catalyzed by $Sb_2(SO_4)_3$.

TABLE II Synthesis of 2,3-Disubstituted Indoles[a]

Entry	R	Ketones	Product	Time (min)	Yields (%)[b]
a	4-H			40	95
b	4-F			50	90
c	4-CH_3			45	88
d	4-OCH_3			20	88
e	2-CH_3			45	70
f	2,5-Cl			130	70
g	4-H			50	95
h	4-F			80	90

(Continued on next page)

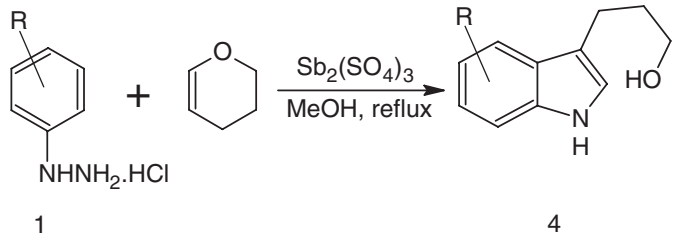
TABLE II Synthesis of 2,3-Disubstituted Indoles[a] *(Continued)*

Entry	R	Ketones	Product	Time (min)	Yields (%)[b]
i	4-CH_3			45	88
j	4-OCH_3			20	90
k	2,5-Cl_2			140	70
l	2-NO_2			150	70
m	CH_3			45	80

[a]Reaction was carried out at reflux temperature in MeOH in presence of 10 mol% of $Sb_2(SO_4)_3$.
[b]Isolated yields.

various phenyl hydrazine hydrochlorides and dihydropyran (Scheme 3); several representative results are summarized in the Table III. In all cases, the reaction of phenylhydrazine hydrochloride with dihydropyran proceeds smoothly at reflux temperature in methanol to produce the corresponding indole-3-propanol in good yield in relatively shorter reaction time.

In conclusion, we have demonstrated that $Sb_2(SO_4)_3$ as an efficient catalyst for the one-pot Fisher indole synthesis. The synthesis of diversely substituted 2,3-disubstituted indoles has shown the wide scope of this reaction. The products are obtained in high yield and good purity.



1 4

SCHEME 3 Synthesis of indoles-3-propanols catalyzed by $Sb_2(SO_4)_3$.

In unsymmetrical case, regiospecific formation of a single product with more substituents in the indole ring is obtained, which indicates that the antimony (III) sulfate provides a weaker acid system for the synthesis of indoles and has a high selectivity as catalyst. The present protocol describes simple isolation and environmentally benign process. The developed method will open new opportunities in the design and synthesis of wide variety of indoles, a structural sub unit of many natural products.

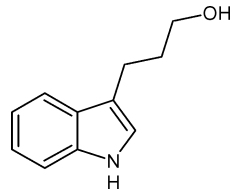
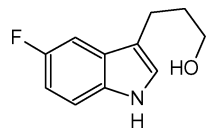
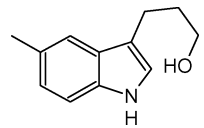
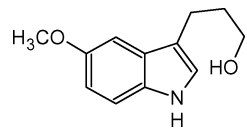
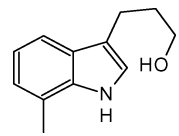
EXPERIMENTAL

All the melting points were recorded in open capillary. The purity of the compounds was checked by TLC on silica gel, and the compounds were purified by column chromatography. ^{1}H NMR spectra were recorded on a Bruker-400 Hz spectrometer using TMS as an internal standard. IR spectra were obtained using a FTS-135 spectrometer instrument. Mass spectra were recorded on a JEOL SX 102/DA-6000 (10 kV) FAB mass spectrometer. The compounds (entries a, e, f, g, k, and m in Table I and entries a–e in Table II) are known, and their identities were proven by means of melting point, IR, ^{1}H NMR, and mass spectra. Herein we give melting points and spectral data for compounds (entries b, c, d, h, i, j, and l in Table I), which could not be found in the literature.

General Procedure for the Synthesis of Indoles

The phenylhydrazine hydrochloride 2.0 g (0.013 mol) and cyclohexanone 1.36 g (0.013 mol) were dissolved in MeOH (20 mL). 20 mol% of $Sb_2(SO_4)_3$ was added to the reaction mixture and refluxed on water bath for the appropriate time (Table II). After the completion of the reaction as indicated by TLC, the reaction mixture was cooled to room temperature and filtered into water (100 mL), and the crude product was extracted with ethyl acetate (2 $\times$ 50 mL). The combined

TABLE III Synthesis of Indole-3-propanol[a]

Entry	R	Product	Time (min)	Yields (%)[b]
a	H		40	92
b	4-F		50	88
c	4-CH_3		45	92
d	4-OCH_3		20	94
e	2-CH_3		45	88

[a]Reaction was carried out at reflux temperature in MeOH in the presence of 10 mol% of $Sb_2(SO_4)_3$.
[b]Isolated yields.

ethyl acetate extracts were washed with water, dried over Na_2SO_4, and evaporated under reduced pressure to provide a crude brown solid. The solid thus obtained was further purified by column chromatography. All other compounds were similarly prepared.

6-Fluoro-2,3,4,9-tetrahydro-1H-carbazole (b: $C_{12}H_{12}FN$)

Crystalline solid, Mp: 93–95°C; IR (KBr): $\bar{V} = 3386$ (NH) cm^{-1}; ^1H NMR (DMSO):$\delta = 10.7$ (br s, NH), 7.2 (dt, 1H,$J = 4.64$), 7.07 (dt, 1H, $J = 2.32$), 6.8 (s, 1H), 2.55–2.72 (m, 4H), 1.74–1.88 (m, 4H); IR 3395; ^{13}C NMR 154.3, 134.5, 132.5, 130.8, 112.5,112.6, 107, 106.6, 35.6, 35,

26.2, 24.5. HRMS: (m/z) = 190.2 (M+1). Anal. Calcd: C (76.17%) H (6.39%) N (7.40%) Found C (77.19%) H (6.45%) N (7.50%).

6-Methyl-2, 3, 4, 9-tetrahydro-1H-carbazole (c: $C_{13}H_{15}N$)

Crystalline solid, Mp: 98–100°C; IR (KBr): $\bar{V}$ = 3394 (NH) cm^{-1}; ^1H NMR (DMSO):δ = 10.4 (br s, NH), 7.1 (dt, 1H, J = 8.6), 6.8 (s, 1H), 6.6 (dt, 1H, J = 2.08), 2.54–2.71 (m, 4H), 2.34 (s, 3H), 1.77–1.96 (m, 4H); IR 3399; ^{13}C NMR 135, 133.2, 131.1, 130.9, 121.2, 120, 112.5, 110.5, 35.3, 35.5, 26.5, 25.2, 21.2. HRMS: (m/z) = 186.2 (M+1). Anal. Calcd: C (84.28%) H (8.16%) N (7.56%). Found C (85.30%) H (9.16) N (7.60%).

6-Methoxy-2, 3, 4, 9-tetrahydro-1H-carbazole (d: $C_{13}H_{15}ON$)

Crystalline solid, Mp: 88–90°C; IR (KBr): $\bar{V}$ = 3381 (NH) cm^{-1}; ^1H NMR (DMSO):δ = 10.4 (br s, NH), 7.1 (dt, 1H, J = 8.6), 6.8 (s, 1H), 6.6 (dt, 1H, J = 2.08), 3.7 (s, 3H), 2.56–2.74 (m, 4H), 1.74–1.94 (m, 4H); IR 3387; ^{13}C NMR 155.2, 135.3, 132.1, 128.2, 112.5, 112.0, 106, 105.2, 55.9, 35.5, 35.3, 26.5, 25.1. HRMS: (m/z) = 202 (M+1). Anal. Calcd: C (77.58%) H (7.51%) N (6.96%). Found C (77.64%) H (8.55%) N (7.01%).

5-Fluoro-2,3-dimethyl-1H-indole (h: $C_{10}H_{10}FN$)

Crystalline solid, Mp: 60–61°C; IR (KBr): $\bar{V}$ = 3364 (NH) cm^{-1}; ^1H NMR ($CDCl_3$):δ = 7.6 (br s, NH), 7.1 (dd, 2H, J = 4.38), 6.8 (t, 1H, J = 2.41), 2.3 (s 3H), 2.1(s, 3H); IR 3394; ^{13}C NMR 155.2, 135.3, 133.1, 131.5, 112.6, 112.5, 107.4,106.5, 8.2, 6.7. HRMS: (m/z) = 164.1 (M+1). Anal. Calcd: C (73.60%) H (6.18%) N (8.58%). Found C (74.50%) H (6.20%) N (8.58%).

2,3,5-Trimethyl-1H-indole (i: $C_{11}H_{13}N$)

Crystalline solid, Mp: 98–99°C; IR (KBr): $\bar{V}$ = 3388 (NH) cm^{-1}; ^1H NMR (DMSO):δ = 10.4 (br s, 1H, NH), 7.1 (dd, 2H, J = 8.9), 6.7 (d, 1H, J = 8.08), 2.3 (s, 3H), 2.2 (s, 3H), 2.1 (s, 3H); IR 3376; ^{13}C NMR 135.2, 133.1, 131.2, 130.5, 121.1, 120.1,112.5,110.6, 21.2, 8.1, 6.6. HRMS: (m/z) = 160 (M+1). Anal. Calcd: C (82.97 %) H (8.23%) N (8.80%). Found C (83.01%) H (8.37) N (9.10%).

5-Methoxy-2,3-dimethyl-1H-indole (j: $C_{11}H_{13}ON$)

Crystalline solid, Mp: 60–61°C; IR (KBr): $\bar{V}$ = 3345 (NH) cm^{-1}; ^1H NMR (DMSO):δ = 10.4 (br s, NH), 7.1 (d, 1H, J = 8.6), 6.8 (s, 1H), 6.6 (d, 1H, J = 2.24), 3.7(s, 3H, -OCH_3), 2.2 (s, 3H), 2.1 (s, 3H); IR 3382; ^{13}C NMR 155.2, 135.2, 132.3, 128.5, 112.5, 112.0, 106.1, 105.1, 56, 8.2, 6.5. HRMS: (m/z) = 176.2 (M+1). Anal. Calcd: C (75.40 %) H (7.48%) N (7.99%). Found C (76.60%) H (7.64) N (8.0%).

7-Nitro-2,3-dimethyl-1H-indole (I: $C_{10}H_{10}O_2N_2$)

Crystalline solid, Mp: 95–96°C; IR (KBr): $\bar{V} = 3378$ (NH) cm^{-1}; ^1H NMR ($CDCl_3$):$\delta = 7.6$ (br s, NH), 7.5 (d, 1H, $J = 7.6$), 7.4 (d, 1H, $J = 8.2$), 7.3 (t, 1H, $J = 8.0$), 2.3 (s, 3H), 2.2 (s, 3H); IR 3368; ^{13}C NMR 135.2, 132.4, 131.2, 130.9, 126.5, 122.6, 114.5, 112.7, 8.2, 6.7. HRMS: (m/z) = 191 (M+1). Anal. Calcd: C (63.15 %) H (5.30%) N (14.73%). Found C (64.24 %) H (6.10%) N (14.96%).

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