

Ring-Opening Cyclization of Cyclohexane-1,3-dione-2spirocyclopropanes with Amines: Rapid Access to 2-Substituted 4-Hydroxyindole

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(5) Supporting Information

ABSTRACT: An efficient ring-opening cyclization of cyclohexane-1,3-dione-2-spirocyclopropanes with primary amines has been developed. The reaction proceeded at room temperature without any additives to provide 2-substituted tetrahydroindol-4-ones in good to excellent yields without the formation of the 3-substituted isomers. The obtained product



was readily converted into a 2-substituted 4-hydroxyindole derivative via a synthetically useful indoline intermediate.

yclopropanes serve as valuable building blocks in organic synthesis.¹ They have strong ring strain, and the relief of the strain provides a high chemical reactivity. Among the large variety of interesting and efficient reactions of cyclopropanes, one of the most extensively investigated reactions is the formal cycloaddition of doubly activated cyclopropanes for the construction of highly functionalized carbo- and heterocyclic compounds,^{2,3} in which ring opening of their cyclopropanes results in the formation of a 1,3-dipole equivalent as a C_3 unit. Another unique application of activated 1-acylcyclopropanes is as C₄ units (from three cyclopropane carbons and one carbonyl carbon); this has been used for the synthesis of heterocycles.^{4–7} Thus, 1-acyl-1-(alkoxycarbonyl)cyclopropanes have been reacted with primary amines at >140 °C to produce 4alkoxycarbonyl-2,3-dihydropyrroles (Scheme 1, eq 1).⁴ Similar reactions using various activating groups such as nitro and cyano groups⁵ and Lewis acid activation⁶ have also been reported. In these reactions, a nucleophilic attack of amine at the doubly activated β -carbon of the acyl group results in formation of a γ -amino ketone, which easily undergoes cyclization to construct the pyrrolidine ring. As an alternative approach, Jabin and co-workers have reported a pyrrole synthesis involving a ring-opening cyclization of a 1,1diacylcyclopropane.⁷ The reaction of a 1,1-diacylcyclopropane with amine in the presence of a catalytic amount of trifluoroacetic acid (TFA) in toluene at reflux provides an α cyclopropyl imine, which when treated with silica gel, followed by air oxidation, gives the corresponding pyrrole through a Cloke-type rearrangement⁸ (Scheme 1, eq 2). These examples offer useful synthetic tools for obtaining nitrogen-containing 5membered rings.

Indoles that possess a cyclohexane-fused pyrrolidine framework are important structural components of a wide range of biologically active alkaloids and pharmaceutical agents.⁹ Although many synthetic methodologies for indoles have been investigated,¹⁰ much effort continues to be devoted to developing efficient synthetic routes, especially to highly

Scheme 1. Ring-Opening Cyclization of Cyclopropanes

A. Previous work: Construction of pyrrole skeletons



Lhommet (1992): EWG = CO_2R ; conditions: MeOH, sealed tube or >140 °C Charette (2005): EWG = NO_{21} CN; conditions: toluene, reflux France (2014): EWG = CO_2Me , COMe; conditions: $Ni(ClO_4)_2$ 6H₂O (15 mol %)



B. This work: Construction of an indole skeleton



substituted indoles.¹¹ As a part of our efforts on the synthesis of functionalized indoles,¹² we investigated the ring-opening cyclization of cyclohexane-1,3-dione-2-spirocyclopropane with primary amines as a new potential route to indole frameworks (Scheme 1, eq 3). Herein, we report that ring-opening cyclizations of cyclohexane-1,3-dione-2-spirocyclopropane with amines proceed smoothly at room temperature without any additives to give 2,3,6,7-tetrahydro-1*H*-indol-4(5*H*)-ones, which are readily converted to highly substituted indoles through the indoline intermediate.

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At the outset of this work, the ring-opening cyclization of spirocyclopropane was explored using the known 6,6-dimethyl-1-phenylspiro[2.5] octane-4,8-dione (1a), readily prepared by Müller's method,¹³ and 1.5 equiv of benzylamine (2a). Among the reported conditions,^{4–7} we first chose the use of Ni(ClO₄)₂. $6H_2O^{14}$ as a catalyst in CH₂Cl₂ at reflux according to France's procedure,⁶ due to the mild conditions at relatively low reaction temperature (Table 1, entry 1). The reaction proceeded with

Table 1. Ring-Opening Cyclization of Spirocyclopropane 1a with Benzylamine $(2a)^{a}$

		BnNH ₂ (2 (1.5 equir Ph additive solvent		J N 3a ^{Bn}	Ph
entry	additive	solvent ^{b} (M)	temp (°C)	time (h)	yield ^c (%)
1	$Ni(ClO_4)_2^d$	CH_2Cl_2 (0.1)	reflux	9	97
2	TFA ^e	toluene (0.1)	reflux	0.5	83
3	MgSO ₄ ^f	CH ₃ CN (0.1)	80	1	95
4		toluene (0.1)	reflux	1	97
5		toluene (0.1)	rt	48	93
6		toluene (0.5)	rt	3	97
7		CH_2Cl_2 (0.5)	rt	3.5	93
8		$CH_{3}CN$ (0.5)	rt	5	97
9		THF (0.5)	rt	3	97
10		THF (0.5)	reflux	0.5	97

^{*a*}All reactions were performed on a 0.2 mmol scale. ^{*b*}Concentration of starting material 1a. ^{*c*}Isolated yield. ^{*d*}A catalytic amount of Ni(ClO₄)₂. 6H₂O (15 mol %) was used. ^{*e*}A catalytic amount of TFA (0.2 equiv) was used. ^{*f*}O.5 equiv of MgSO₄ was used.

ring-opening and cyclization, and 2-phenyl-substituted tetrahydroindol-4-one 3a was obtained after 9 h in 97% yield with no evidence of the formation of the 3-phenyl-substituted product. Next, we tested the formation of the imine according to Jabin's method (entry 2).⁷ Unexpectedly, the reaction of 1a in the presence of a catalytic amount of TFA in toluene at reflux afforded, in 83% yield, the cyclization product 3a, not the corresponding imine product. The use of MgSO₄ as a desiccant in CH₃CN at 80 $^{\circ}C^{15}$ resulted in a high yield of 3a (95% yield, entry 3). Since ring-opening reactions of doubly activated cyclopropane under heating conditions were reported by Lhommet⁴ and Charette⁵ (Scheme 1, eq 1), the reaction in toluene at reflux was examined (entry 4). As a result, a high product yield of 3a was obtained without any additives (97% yield). To our surprise, the reaction proceeded at room temperature to afford 3a in 93% yield, although a much longer reaction time (48 h) was needed to reach completion (entry 5). Remarkably, the reaction at a higher molar concentration of 1a (0.5 M) shortened the reaction time to 3 h and led to high yield of 3a (97% yield, entry 6). In contrast to the ring-opening of nonspirocyclopropanes which required further activation or heating conditions,^{4–7} **1a** does not need any activation due to the spiro activation.^{1b} A survey of solvents revealed that toluene and THF were suitable for this reaction in terms of product yield and reaction rate (entries 6-10).

Having optimized the reaction conditions, we investigated the reaction of 1a with a range of amines 2 in THF (Table 2). The use of *p*-methoxybenzylamine (PMBNH₂, 2b), allylamine (2c) and *n*-butylamine (2d) regioselectively afforded the corresponding 2-phenyl-substituted products 3b, 3c, and 3d Table 2. Ring-Opening Cyclization of Spirocyclopropane 1a with a Variety of Amines 2^a

		RNH ₂ : (1.5 equ Ph THF, r	$t \rightarrow t$	∼ N R	
		amine	_		
entry		R	time (h)	yield	^b (%)
1	2b	PMB	3	3b	92
2	2c	allyl	5	3c	98
3	2d	"Bu	2.5	3d	95
4	2e	^t Bu	60	3e	85
5	2f	Ph	4	3f	64
6 ^{<i>c</i>}	2f	Ph	2	3f	76
7	2g	4-MeOC ₆ H ₄	4	3g	39
8 ^c	2g	$4-MeOC_6H_4$	1	3g	86
9	2h	H^d	2	3h	31
10	2i	Cbz	24		

^{*a*}All reactions were performed on a 0.2 mmol scale. ^{*b*}Isolated yield. ^{*c*}These reactions were conducted in toluene at 70 °C. ^{*d*}10 equiv of ammonia solution (25% in water) was used. PMB: *p*-methoxybenzyl.

in 92%, 98%, and 95% yields, respectively (entries 1–3). The reaction with *tert*-butylamine (2e) as a sterically hindered amine resulted in good yield of 3e, but a significantly longer time was required to reach completion (60 h, 85% yield, entry 4). In the case of aromatic amines such as aniline (2f) and *p*-anisidine (2g), moderate product yields (39–64% yields) were obtained owing to the formation of several side products (entries 5 and 7). Gratifyingly, switching the solvent to toluene and heating at 70 °C greatly improved the product yields, providing the dihydropyrroles 3f and 3g in 76% and 86% yields, respectively (entries 6 and 8). The use of ammonia solution (25% in water) afforded the *N*-unprotected product 3h in moderate yield (31% yield, entry 9). The reaction with CbzNH₂ and the corresponding amide prepared with NaH did not give the desired product (entry 10).

Using benzylamine (2a) as an amine nucleophile, we explored the scope of the reaction with respect to the substituents on the cyclopropane (Table 3). The reaction of p-tolyl-substituted cyclopropane 1b proceeded smoothly to completion within 2.5 h, giving the 2-substituted tetrahydroindol-4-one 3i as the sole product in 86% yield (entry 1). The use of 1-aryl-substituted spirocyclopropanes 1c and 1d with a chlorine atom present at the para- and ortho-positions on the benzene ring provided the corresponding products 3j and 3k in 97% yield (entries 2 and 3). The reaction of cyclopropane 1e, bearing a 2,3,4,5,6-pentafluorophenyl group, resulted in a good yield of 3l, although the reaction time was prolonged (48 h, 90% yield, entry 4). The use of cyclopropane 1f, possessing an alkyl substituent on the cyclopropane ring, led to a high yield of 3m (97% yield), but the reaction time was much longer (168 h) than those with aromatic substituents (entry 5). As might be expected, the reaction of 1f in THF at reflux reduced the reaction time (8 h) and provided 3m in 96% yield.¹⁶ The ring-opening cyclization of simple cyclopropane substrate 1g¹⁷ proceeded uneventfully and afforded the desired product 3n in 92% yield (entry 7).

A plausible mechanism for the ring-opening cyclization of spirocyclopropane 1 with amine 2 is shown in Scheme 2. On the basis of previous reports, $^{4-7}$ two routes to the 2-substituted

Table 3. Ring-Opening Cyclization of a Variety of Spirocyclopropanes 1b-g with Benzylamine $(2a)^a$



^{*a*}All reactions were performed on a 0.2 mmol scale with 1.5 equiv of benzylamine (2a) in THF at room temperature. ^{*b*}Isolated yield. ^{*c*}The reaction was conducted in THF at reflux.

Scheme 2. Plausible Mechanism



tetrahydroindol-4-one 3 are proposed. In one route (route a), ring-opening of the spirocyclopropane 1 proceeds through an S_N 2-like displacement by the nucleophilic amine 2 at the more electrophilic substituted carbon on the cyclopropane A,⁵ leading to γ -amino ketone 4 regioselectively. Nucleophilic attack of amine to the carbonyl carbon 4 followed by dehydration of hemiaminal 5 provides tetrahydroindol-4-one 3. An alternative route employing imine rearrangement^{8,18} is also proposed (route b). However, the present reaction would proceed through γ -amino ketone 4 (route a) because the corresponding imine product **6** could not be detected even with a catalytic amount of TFA (Table 1, entry 2).⁷

Using the present protocol, we prepared the 4-hydroxyindole

8 (Scheme 3). Ring-opening cyclization of spirocyclopropane

Scheme 3. Synthesis of 4-[(*tert*-Butyldimethylsilyl)oxy]indole 8 from Spirocyclopropane 1h



1h, prepared from 2-diazocyclohexane-1,3-dione and styrene according to the procedure of Müller,¹³ with **2a** proceeded smoothly at room temperature to give tetrahydroindol-4-one **3o** in 95% yield. According to the literature procedure,¹⁹ bromination of **3o** with CuBr₂ in EtOAc at reflux was followed by aromatization using a combination of LiBr and Li₂CO₃ to afford 4-hydroxyindoline 7 in 82% yield. Since indoline is a ubiquitous scaffold found in a large range of biologically active alkaloids and pharmaceutically active compounds,²⁰ this synthetic route to indoles via indoline intermediates offers a distinctive advantage. While dehydrogenation of indoline 7 possessing a free phenolic hydroxyl group gave a complex mixture of products, oxidation of *tert*-butyldimethylsilyl (TBS)-protected 4-hydroxyindoline with chloranil furnished 4-hydroxyindole derivative **8** in 87% yield from 7.

In conclusion, we have developed a regioselective ringopening cyclization of cyclohexane-1,3-dione-2-spirocyclopropanes with primary amines. The reaction proceeds at room temperature without any additives to provide tetrahydroindol-4-ones in good-to-excellent yields. To the best of our knowledge, this is the first example of the synthesis of indole frameworks using the ring-opening reaction of cyclopropanes. The present protocol is applicable to the synthesis of 2substituted 4-hydroxyindoles via a synthetically useful indoline intermediate. Further application of this method to the synthesis of biologically active indole alkaloids as well as mechanistic studies are currently in progress.

ASSOCIATED CONTENT

S Supporting Information

Experimental procedures, characterization data, and 1 H and 13 C NMR spectra for new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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