PPh 2 Me-Mediated Tandem Reaction of 2-Alkyl-2,3-butadienoates with Isothiocyanates: Formation of 2-Aminothiophenes

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PPh_2Me-Mediated Tandem Reaction of 2-Alkyl-2,3-butadienoates with Isothiocyanates: Formation of 2-Aminothiophenes

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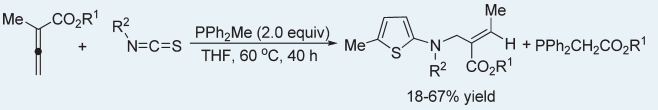
Supporting Information

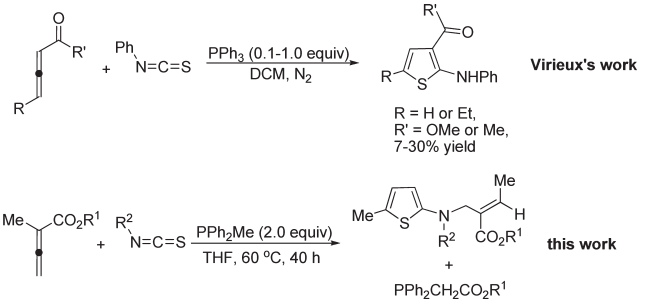
ABSTRACT: 2-Aminothiophenes were obtained through a PPh_2Me-mediated tandem reaction of 2-alkyl-2,3-butadienoates with isothiocyanates, which involves an annulation of 2-alkyl-2,3-butadienoates with isothiocyanates and a subsequent umpolung addition to 2-alkyl-2,3-butadienoates.



KEYWORDS: allenoate, isothiocyanate, 2-aminothiophene, annulation, umpolung addition

Recently, the phosphine-catalyzed annulation reactions of allenoates with electron-deficient olefins or imines have received considerable research interest,[1−5] since Lu's pioneering reports on [3 + 2] cycloaddition reactions[6−11] between allenoates and imines or electron-deficient olefins catalyzed by tertiary phosphines, because these are highly attractive synthetic methods for preparing a variety of carbocycles and heterocycles from readily available starting materials. At the same time, the asymmetric [3 + 2] cycloaddition reactions[12−18] between allenoates and imines or electron-deficient olefins catalyzed by chiral tertiary phosphines have also been developed significantly. With the aim of developing new phosphine-catalyzed cycloaddition reactions of allenoates, much effort has been devoted to investigate the [3 + 2] cycloaddition reactions of allenoates with different kinds of electron-deficient olefins, such as arylmethylidenemalononitriles and nitroalkenes.[19,20] Furthermore, to extend the scope of electron-deficient olefins or allenes involving [3 + 2] cycloaddition reactions, in 2006, Virieux[21] reported a novel PPh_3-catalyzed [3 + 2] cycloaddition reaction of phenyl isothiocyanate with electron-deficient allenes, which offered a new way to synthesize 2-aminothiophenes.[22,23] However, the isolated yields of products remained low in all tested conditions (Scheme 1). On the other hand, 2-alkyl-2,3-butadienoates have been employed in the phosphine-catalyzed [4 + 2] cycloaddition reactions with imines or arylmethylidenemalononitriles by Kwon.[24−28] These reactions underwent a different reaction pathway, suggesting that the subtle structural changes in allenoates could significantly alter the reaction pathway. These works aroused our enthusiasm to study the reactions of 2-alkyl-2,3-butadienoates with isothiocyanates catalyzed by phosphines. Unexpectedly, we found a tandem reaction of annulation and a subsequent umpolung addition using 2-alkyl-2,3-butadienoates and isothiocyanates as the substrates, giving the corresponding 2-aminothiophene derivatives in moderate yields under mild conditions (Scheme 1). Herein, we report the details of this novel tandem reaction of 2-alkyl-2,3-butadienoates with isothiocyanates mediated by phosphines.

Scheme 1. Phosphine-Catalyzed or -Mediated Annulation Reactions of Isothiocyanates with Electron-Deficient Allenes



Initially, the reaction of ethyl 2-methyl-2,3-butadienoate **1a** with phenyl isothiocyanate **2a** (1:1) was conducted at room temperature in the presence of PBu_3 (20 mol %) in dichloromethane (DCM), affording an unexpected new product **3a** in 19% yield (Table 1, entry 1). Through a series of analytical measurements, compound **3a** was identified as a tandem reaction product of annulation and a subsequent umpolung addition between two molecules of ethyl 2-methyl-2,3-butadienoate **1a** and one molecule of phenyl isothiocyanate **2a**. The product **3a** was also a 2-aminothiophene derivative, but one CO_2Et group was eliminated during the reaction, which was different from Virieux's work mechanistically.[21] To understand the reason for the elimination of the CO_2Et group and to improve the yield of **3a**, we increased the employed amount of PBu_3 to 1.0 equiv and changed the ratio of ethyl 2-methyl-2,3-butadienoate **1a** and phenyl isothiocyanate **2a** to 2:1, but **3a** was still obtained in low yield (Table 1, entry 2).

Next, the potential of several commonly used phosphines was assessed as the catalysts for the tandem reaction of ethyl

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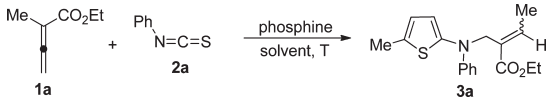
Table 1. Phosphine and Solvent Screening for the Reaction of Ethyl 2-Methyl-2,3-butadienoate 1a with Phenyl Isothiocyanate 2a



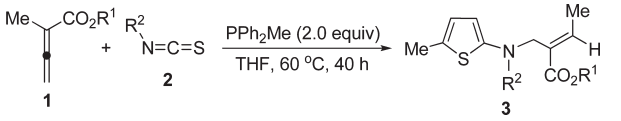
entry[a]	solvent	phosphine	1a:2a	T (°C)	time (h)	yield (%)[b]	E/Z[c]
1	DCM	PBu_3(0.2 equiv)	1:1	rt	24	(19)	
2	DCM	PBu_3(1.0 equiv)	2:1	rt	24	(13)	
3	THF	PBu_3(1.0 equiv)	2:1	60	40	(10)	
4	THF	PMe_3 (1.0 equiv)	2:1	60	40	(8)	
5	THF	$PPhMe_2$ (1.0 equiv)	2:1	60	40	(15)	
6	THF	PPh_2Me (1.0 equiv)	2:1	60	40	(24)	
7	THF	PPh_2Me (1.0 equiv)	1:2	60	40	69	6.6:1
8	THF	PPh_2Me (1.5 equiv)	1:2	60	40	72	7.8:1
9	THF	PPh_2Me (2.0 equiv)	1:2	60	40	79 (67)	7.4:1
10	THF	PPh_2Me (0.5 equiv)	1:2	60	40	47	6.1:1
11	THF	dppe (1.0 equiv)	1:2	60	40	24	3.1:1
12	THF	dppb (1.0 equiv)	1:2	60	40	49	6.5:1
13	toluene	PPh_2Me (2.0 equiv)	1:2	60	48	73 (57)	6.3:1
14	dioxane	PPh_2Me (2.0 equiv)	1:2	60	48	63	7.9:1
15	CH_3CN	PPh_2Me (2.0 equiv)	1:2	60	48	13	
16	DCE	PPh_2Me (2.0 equiv)	1:2	60	48	44	9.4:1
17	DCM	PPh_2Me (2.0 equiv)	1:2	rt	48	64	14.2:1
18	THF	PPh_2Me (2.0 equiv)	1:2	rt	48	45	11.3:1
19	THF	PPh_2Me (2.0 equiv)	1:1	60	40	67	6.2:1
20[d]	THF	PPh_2Me (2.0 equiv)	1:2	60	40	77 (57)	8.6:1
21[e]	THF	PPh_2Me (2.0 equiv)	1:2	60	40	45	15.1:1

[a] Reaction conditions: (A) **1a** (0.2 mmol), **2a** (0.4 mmol), and phosphine (0.2 mmol) in 2.0 mL of solvent; (B) **1a** (0.2 mmol), **2a** (0.1 mmol), and phosphine (0.2 mmol) in 2.0 mL of solvent; (C) **1a** (0.2 mmol), **2a** (0.2 mmol), and phosphine (0.2 mmol) in 2.0 mL of solvent. [b] Yields were determined by ^{1}H NMR spectrum with 1,3,5-trimethoxybenzene as the internal standard. In parentheses are the isolated yields of the *E* isomer. [c] Determined by ^{1}H NMR spectrum. [d] In 4.0 mL of THF. [e] In 1.0 mL of THF.

2-methyl-2,3-butadienoate **1a** with phenyl isothiocyanate **2a** in THF at 60 °C. However, the yields of **3a** were still low (Table 1, entries 3−6). Using PPh_2Me as the catalyst, a byproduct was isolated, and its structure was assigned as $PPh_2CH_2CO_2Et$. According to this result, we could know that a CO_2Et group was removed by the phosphine catalyst, and this tandem reaction was not a phosphine-catalyzed reaction; it was a phosphine-mediated reaction. When the ratio of ethyl 2-methyl-2,3-butadienoate and phenyl isothiocyanate was changed to 1:2, **3a** could be obtained in 69% yield using 1.0 equiv of PPh_2Me at 60 °C (Table 1, entry 7). Increasing the amount of PPh_2Me to 1.5 or 2.0 equiv, the yield of **3a** was improved to 72% and 79%, respectively, with 67% isolated yield of (*E*)-**3a** (Table 1, entries 8 and 9). 1,2-Bis(diphenylphosphino)ethane (dppe) and 1,2-bis(diphenylphosphino)butane (dppb), which have structures similar to PPh_2Me, were also examined in this reaction, but they did not improve the reaction outcomes (Table 1, entries 11 and 12).

The solvent effects were next examined using PPh_2Me as the catalyst. Toluene was also a suitable solvent to give **3a** in 73% yield along with 57% isolated yield of (*E*)-**3a** (Table 1, entry 13).

Table 2. PPh2Me-Mediated Reaction of 2-Methyl-2,3-butadienoate 1 with Isothiocyanates 2



entry[a]	1:2	R^1	R^2	yield (%)[b]
1	1:2	Et, **1a**	4-$MeOC_6H_4$, **2b**	**3b**, 43
2	2:1	Et, **1a**	4-$MeOC_6H_4$, **2b**	**3b**, 52
3	2:1	Et, **1a**	4-ClC_6H_4, **2c**	
4	2:1	Et, **1a**	3-MeC_6H_4, **2d**	**3d**, 33
5	2:1	Et, **1a**	4-MeC_6H_4, **2e**	**3e**, 46
6	2:1	Et, **1a**	2-$MeOC_6H_4$, **2f**	**3f**, 23
7	2:1	Et, **1a**	2-MeC_6H_4, **2g**	**3g**, 30
8	2:1	Et, **1a**	Bn, **2h**	**3h**, 30
9	1:2	Et, **1a**	Bn, **2h**	**3h**, 43
10	1:2	Et, **1a**	Ph_2CH, **2i**	**3i**, 62
11	1:2	Et, **1a**	4-$MeOC_6H_4CH_2$, **2j**	**3j**, 28
12	2:1	Me, **1b**	Ph, **2a**	**3k**, 53
13	2:1	Me, **1b**	4-$MeOC_6H_4$, **2b**	**31**,45
14	2:1	^{i}Pr, **1c**	Ph, **2a**	**3m**, 67
15	2:1	^{i}Pr, **1c**	4-$MeOC_6H_4$, **2b**	**3n**, 45
16	2:1	Bn, **1d**	Ph, **2a**	**3o**, 31
17	2:1	Bn, **1d**	4-$MeOC_6H_4$, **2b**	**3p**, 18
18	2:1	Ph, **1e**	Ph, **2a**	
19	2:1	Ph, **1e**	4-$MeOC_6H_4$, **2b**	

[a] Reaction conditions: (A) **1** (0.2 mmol), **2** (0.4 mmol), and PPh_2Me (0.2 mmol) in 2.0 mL of THF; (B) **1** (0.2 mmol), **2** (0.1 mmol) and PPh_2Me (0.2 mmol) in 2.0 mL of THF. [b] Isolated yields of *E* isomers.

Decreasing the temperature to room temperature afforded **3a** in lower yield (Table 1, entry 18). Adjusting the reaction concentration could also affect the reaction outcome, and we found that **3a** could be obtained in higher yield (77% yield) under diluted reaction conditions (Table 1, entries 20 and 21). It should be mentioned that all the isolated yields of product **3** are based on 2-methyl-2,3-butadienoate **1** because isothiocyanate still remained after a prolonged reaction time in the reaction of butadienoate and isothiocyanate with a 1:2 or 2:1 ratio.

Having identified the optimal reaction conditions, we next set out to examine the scope and limitations of this reaction using various isothiocyanates **2** bearing different substituents, and the results are summarized in Table 2. As shown in Table 2, when the ratio of ethyl 2-methyl-2,3-butadienoate **1a** and isothiocyanate **2b** was 1:2, the product **3b** was obtained in 43% yield (Table 2, entry 1). However, when the ratio of **1a** and **2b** was 2:1, **3b** was isolated in higher yield (Table 2, entry 2). With a 2:1 ratio of ethyl 2-methyl-2,3-butadienoate **1a** and isothiocyanates **2**, some other aryl isothiocyanates were employed in this reaction.

Isothiocyanates **2** having electron-donating group at ortho, meta, or para positions of their benzene rings could give the corresponding 2-aminothiophene products in 23−46% yields along with some unidentified byproducts (Table 2, entries 4−7). Isothiocyanates with an electron-withdrawing group at the benzene rings, such as **2c**, did not give the corresponding 2-aminothiophene product (Table 2, entry 3). When benzyl isothiocyanate **2h** was employed as substrate, the corresponding product **3h** was obtained in higher yield because the ratio of **1a** and **2h** was 1:2 (Table 2, entries 8 and 9).

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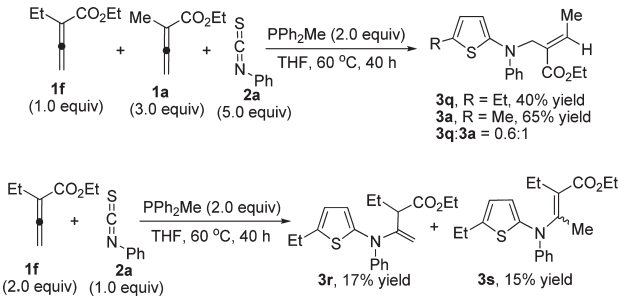
Scheme 2. PPh_2Me-Mediated Reaction of Ethyl 2-Ethyl-2,3-butadienoate 1b with Phenyl Isothiocyanate 2a



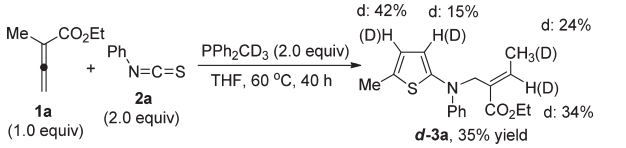
Keeping the ratio of **1a** and alkyl isothiocyanates **2** at 1:2, several other alkyl isothiocyanates were also examined in this reaction. The corresponding 2-aminothiophene derivatives **3i** and **3j** could be obtained in 62 and 28% yields, respectively, under the standard conditions (Table 2, entries 10 and 11). Since the yields of products **3** were not satisfactory, according to the structure of product **3** and the byproduct $PPh_2CH_2CO_2Et$, we considered that CO_2Et was eliminated during the reaction and the ester groups of 2-methyl-2,3-butadienoates might have an effect on the formation of 2-aminothiophene product **3**.

Some other 2-methyl-2,3-butadienoates **1b**, **1c**, and **1d** with different ester groups were synthesized and used in the reaction with isothiocyanates **2a** and **2b**, respectively, with the ratio of **1** and **2** being 2:1. Unfortunately, no improvement was observed, and results similar to those of **1a** were obtained under the optimal conditions (Table 2, entries 12−17). Phenyl 2-methyl-2,3-butadienoate **1e** did not react with **2a** or **2b** to give the corresponding 2-aminothiophene derivative (Table 2, entries 18 and 19).

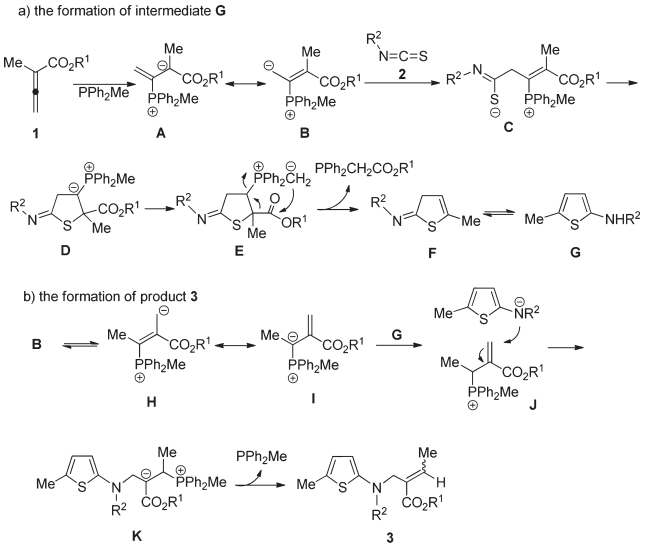
In addition to the scope of isothiocyanates, some other 2-alkyl-2,3-butadienoates were also explored for this reaction. The results are listed in Scheme 2. According to our previous report[29] on the phosphine-catalyzed umpolung addition reaction of nucleophiles to ethyl 2-methyl-2,3-butadienoate,[30] nucleophiles could not add to the α-methylene group of ethyl 2-ethyl-2,3-butadienoate **1f**. Thus, at the beginning, we anticipated that the reaction of ethyl 2-ethyl-2,3-butadienoate **1f** and isothiocyanates might not take place due to the unsuccessful umpolung addition reaction of nucleophiles to ethyl 2-ethyl-2,3-butadienoate. However, it was found that when both ethyl 2-methyl-2,3-butadienoate **1a** and ethyl 2-ethyl-2,3- butadienoate **1f** were employed in the reaction with phenyl isothiocyanate **2a** under the optimal reaction conditions, a product mixture of **3a** and **3q** could be isolated in 65% and 40% yields, respectively (Scheme 2). Obviously, product **3q** was formed by the annulation of ethyl 2-ethyl-2,3-butadienoate **1f** with phenyl isothiocyanate **2a** and a subsequent umpolung addition to ethyl 2-methyl-2,3-butadienoate **1a**. Next, the reaction of ethyl 2-ethyl-2,3-butadienoate **1f** with phenyl isothiocyanate **2a** was carried out, and we found that products **3r** and **3s** could be isolated in 17% and 15% yield, respectively (Scheme 2). Products **3r** and **3s** were formed through the annulation of ethyl 2-ethyl-2,3-butadienoate **1f** with phenyl isothiocyanate **2a** and a subsequent Michael addition to ethyl 2-ethyl-2,3-butadienoate **1f**.

To gain more mechanistic insights into the reaction, some isotope labeling experiments were conducted (Scheme 3). Using PPh_2CD_3 as the promoter, the corresponding deuterated product *d*-**3a** could be obtained in 35% yield. Deuterium was incorporated

Scheme 3. Isotope Labeling Experiments



Scheme 4. Plausible Reaction Mechanism



into the 3- and 4-positions of the thiophene ring, the methyl group, and the alkene hydrogen atom connected to the double bond at ratios of 15%, 42%, 24% and 34%, respectively (Scheme 3).

On the basis of the above results and the previous literature,[21,29−32] a plausible mechanism for this PPh_2Me-mediated reaction between 2-methyl-2,3-butadienoates and isothiocyanates is proposed in Scheme 4. The Lewis base PPh_2Me as a nucleophile reacts with 2-methyl-2,3-butadienoates to produce the corresponding zwitterionic intermediate **A**, which exists as a resonance-stabilized zwitterionic intermediate **A** (enolate) and intermediate **B** (allylic carbanion). The carbon anion in intermediate **B** adds nucleophilically to isothiocyanate **2** to give intermediate **C**, which undergoes an intramolecular nucleophilic addition to afford intermediate **D**. Intermediate **D** can be further transformed to intermediate **E** through a proton shift. The carbon anion in intermediate **E** adds to the ester group, and moreover, the elimination of $PPh_2CH_2CO_2R^1$ furnishes intermediate **F**, which can isomerize to intermediate **G**. Meanwhile, intermediate **B** can be further transformed to intermediate **H** through a 1,4-hydrogen shift or a two-step proton transfer process, and the corresponding resonance-stabilized zwitterionic intermediate **I**. The succeeding mechanism is similar to our previous report,[29] in which intermediate **G** as the nucleophile undergoes a phosphine-catalyzed umpolung addition reaction to the α-methyl group of ethyl 2-methyl-2,3-butadienoate to give the corresponding intermediates. Concretely, intermediate **I** deprotonates intermediate **G** to generate intermediate **J** and the corresponding nucleophilic anion, which undergoes a subsequent addition to intermediate **J** to afford intermediate **K**. Subsequently, the elimination of PPh_2Me from intermediate **K** furnishes the corresponding product and regenerates the phosphine catalyst.

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According to this plausible reaction mechanism, the results of isotope labeling experiments could be successfully rationalized. The deuterium at the 4-position of thiophene ring was incorporated through the proton shift from intermediate **D** to intermediate **E**. On the other hand, it was also found that the deuterium in $PPh_2CD_2CO_2Et$ could easily undergo proton-exchange with active hydrogen atoms in other intermediates, such as intermediate **G** (see the Supporting Information). The amino hydrogen atom in intermediate **G** undertook proton exchange with $PPh_2CD_2CO_2Et$ to form deuterated intermediate **G**, which could introduce deuterium to the 3-position of thiophene ring through tautomerization with intermediate **F**. The deuterated intermediate **G** could also introduce deuterium to the alkene hydrogen atom through the deprotonation process from intermediate **I** to intermediate **J**. The deuterium in the methyl group could be introduced by the proton shift among the intermediates **A**, **B**, **H**, or **I**, in which the deuterium in the CD_3 group of the phosphonium might join in the proton shift.

In summary, we have developed a novel PPh2Me-mediated tandem reaction of 2-alkyl-2,3-butadienoates with isothiocyanates in which 2-aminothiophenes could be obtained through an annulation of 2-alkyl-2,3-butadienoates with isothiocyanates and a subsequent umpolung addition to 2-alkyl-2,3-butadienoates. In the annulation of 2-alkyl-2,3-butadienoates with isothiocyanates, one ester group of 2-alkyl-2,3-butadienoates was eliminated to form $PPh_2CH_2CO_2R$. Efforts are in progress to elucidate further mechanistic details of these reactions and to explore the scope and limitations of the other coupling reactions between isothiocyanates and allenoates.

EXPERIMENTAL SECTION

General Procedure for the PPh_2Me-Mediated Reaction of Ethyl 2-Methyl-2,3-butadienoate 1 with Isothiocyanate 2. Procedure A: Isothiocyanate **2** (0.4 mmol) was dissolved in THF (2.0 mL) in a 10-mL Schlenk flask containing a stir bar. The solution was degassed using a freeze−pump−thaw method over three cycles and allowed to warm to room temperature. Then 2-methyl-2,3-butadienoate **1** (0.2 mmol) and PPh_2Me (0.2 mmol) were introduced successively under argon atmosphere. After the reaction mixture was stirred at 60 °C for 40 h, the solvent was removed under reduced pressure, and the residue was purified by flash column chromatography (SiO_2; eluent: EtOAc/petroleum ether = 1/100) to yield the corresponding product **3**.

Procedure B: Isothiocyanate **2** (0.1 mmol) was dissolved in THF (2.0 mL) in a 10-mL Schlenk flask containing a stir bar. The solution was degassed using a freeze−pump−thaw method over three cycles and allowed to warm to room temperature. Then 2-methyl-2,3-butadienoate **1** (0.2 mmol) and PPh_2Me (0.2 mmol) were introduced successively under argon atmosphere. After the reaction mixture was stirred at 60 °C for 40 h, the solvent was removed under reduced pressure, and the residue was purified by flash column chromatography (SiO_2; eluent: EtOAc/petroleum ether = 1/100) to yield the corresponding product **3**.

ASSOCIATED CONTENT

Supporting Information. ^1H NMR and ^{13}C NMR spectroscopic and analytic data of the compounds **3** as well as the deuterium labeling experiments are included. This material is available free of charge via the Internet at http://pubs.acs.org.)

AUTHOR INFORMATION

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