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Iodine-Catalyzed Aziridination of Alkenes using Chloramine-T as a Nitrogen Source

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Abstract: Iodine was found to be an efficient catalyst for the aziridination of alkenes utilizing Chloramine-T (*N*-chloro-*N*-sodio-*p*-toluenesulfonamide) as a nitrogen source. For example, when two equivalents of styrene were added to Chloramine-T in the presence of a catalytic amount of iodine in a 1:1 solvent mixture of acetonitrile and neutral buffer, the corresponding aziridine 1 was obtained in 91% yield. The reaction could be applied to other acyclic and cyclic alkenes such as 1-octene and cyclohexene. The aziridination of *p*-substituted styrene derivatives 2-5 with Chloramine-T showed that electron-rich alkenes reacted faster than electron-poor ones. Several Chloramine-T analogs were also examined and were found to give the corresponding aziridines 8-10 in only moderate yields. © 1998 Elsevier Science Ltd. All rights reserved.

INTRODUCTION

Chloramine-T, which is a well-known commercially available oxidizing reagent, serves as sources of chloronium cation and/or nitrogen anion, and is also used extensively in analytical chemistry.¹ As a result, synthetic applications of Chloramine-T have been developed by utilizing its reactivity toward a wide variety of functional groups.¹ The representative examples of typical reactions are as follows. Aminochalcogenation proceeds via the reaction of alkenes with the species derived from Chloramine-T and diphenyl disulfide or diphenyl diselenide (eq 1).² Selenium diimide, which is readily prepared by the reaction of Chloramine-T with selenium metal, is used in the allylic amination of aliphatic alkenes (eq 2)³ and also reacts with dienes to give diamine derivatives (eq 3).⁴ The most impressive methodology utilizing Chloramine-T, which has been reported by Sharpless and his co-workers, is the vicinal aminohydroxylation of alkenes by the reagent in the presence of a catalytic amount of osmium tetraoxide. Recently this method has been elegantly extended to practical asymmetric synthesis (eq 4).^{5,6}

Aziridines are useful synthetic intermediates, which can be used in the preparation of nitrogen-containing functional compounds via ring opening and ring expansion reactions.⁷ They are also found in some natural products as well as biologically active compounds such as mitomycins and azinomycins.^{7,8} Although a variety of routes leading to aziridines have been developed to date, with the exception of our recent report (eq 5),⁹ no

examples of aziridination using Chloramine-T have appeared. This new synthetic transformation involves the CuCl-catalyzed aziridination utilizing Chloramine-T, but the yields of aziridines are moderate. In order to improve the yields, we examined other catalysts and found iodine to be a highly effective catalyst for the aziridination of alkenes. In this paper we report the aziridination of alkenes utilizing a Chloramine-T/iodine system, which includes optimization of the reaction conditions and the extension of this to a variety of alkenes.



RESULTS AND DISCUSSION

Although the aziridination of alkenes using primary amines and iodine has been reported,¹⁰ the method suffers from the following restrictions: 1) A stoichiometric amount of iodine is required. 2) The alkene substrates are limited to α , β -unsaturated ketones. In preliminary experiments, the aziridination of unfunctionalized alkenes with a catalytic amount of iodine was carried out utilizing Chloramine-T as a nitrogen source. When two equivalents of styrene were added to a suspension of Chloramine-T in acetonitrile in the presence of a catalytic amount of iodine, *N*-(*p*-toluenesulfonyl)-2-phenylaziridine (1) was obtained in 76% yield (eq 6).

The results of the aziridination of styrene under a variety of conditions are listed in Table 1. When a 1:1 mixture of acetonitrile and neutral buffer (pH 6.86; phosphate buffer) was employed as the solvent for the reaction, because of the poor solubility of Chloramine-T in acetonitrile, the aziridination of styrene proceeded in excellent yield (91%). When a basic (pH 9.18; tetraborate buffer) or acidic buffer (pH 4.01; phthalate buffer) was used in place of neutral buffer solution, the results were less effective. The use of other organic solvents,

which are capable of dissolving Chloramine-T in water, such as 'BuOH, EtOH or DMF afforded moderate yields of 1, while no reaction was observed for the cases of benzene, ether or dichloromethane.

run	solvent	styrene / equiv	time / h	yield / % ^a
1	MeCN	2	24	76
2	MeCN / neutral buffer ^b (1/1)	2	10	91 ^c
3	MeCN / neutral buffer (1/1)	1.5	24	72
4	MeCN / neutral buffer (1/1)	1	24	60
5	MeCN / basic buffer ^d (1/1)	2	10	82
6	MeCN / acidic buffer ^e (1/1)	2	10	76
7	^t BuOH / neutral buffer (1/1)	2	10	74
8	EtOH / neutral buffer (1/1)	2	10	44
9	DMF / neutral buffer (1/1)	2	10	34

Table 1. Aziridination of styrene using the I₂-Chloramine-T system.

^a ¹H-NMR yield based on Chloramine-T. ^b pH 6.86; Phosphate pH standard solution. ^c Isolated yield. ^d pH 9.18; Tetraborate pH standard solution. ^e pH 4.01; Phthalate pH standard solution.

In order to examine the electronic effect of alkenes on reactivity, the reaction of a variety of p-substituted styrene derivatives were examined. The time courses for the aziridination of each styrene derivative was monitored by HPLC and the results are shown in Figure 1. The reaction rate for p-nitrostyrene was conspicuously slower than that of styrene and the yield was low. p-Chlorostyrene also reacted slowly with Chloramine-T to give a moderate yield of the corresponding aziridine. Although the initial reaction rates of both p-methylstyrene and styrene were nearly the same, the final yield of 4 (X = Me) was lower than that of 1 (X = H) after a 10 h reaction. It is noteworthy that the reaction of p-methoxystyrene was very rapid, but a gradual decomposition of the product was observed after 1 h. Subsequent experiments showed that the aziridination rates of electron-rich alkenes were higher than those of electron-poor ones under the same conditions.

The influence of the amount of iodine as a catalyst was evaluated using styrene as a representative model. When the aziridination of styrene was examined using iodine over a range of 5-100 mol%, followed by analysis of the reaction products by HPLC, a unique phenomenon was observed (Figure 2). The rate for the reaction was very small when 5 mol% iodine was used. Unexpectedly, increasing the amount of iodine to 20 mol% caused a slight decrease in the yield compared to the case where 10 mol% of iodine was used. The yield of aziridine in the presence of 20 mol% of iodine did not change even when the reaction time was extended from 10 h to 24 h. However, the gradual decomposition of the product was observed when 50 mol% of iodine was used. Aziridination with an equimolar amount of iodine caused a dramatic decrease in the desired product and two other products were isolated after 10 h (eq 7). The major product derived from styrene was 2-iodo-1-phenylethanol (6), the formation of which suggests the existence of iodonium intermediate in this system. The other product, N-(p-toluenesulfonyl)-2-amino-1-phenylethanol (7), represents a decomposition product of the aziridine.



Figure 1. Time course for the aziridination of *p*-substituted styrene derivatives.



Figure 2. Time course for the aziridination of styrene using various amounts of I₂.



We also examined some Chloramine-T analogs in the aziridination reaction (Table 2). The aziridination of styrene using Chloramine-B, which contains no substituent on the benzene ring, as a nitrogen source afforded the corresponding aziridine 8 in 73% yield (run 2). *p*-Nitro-substituted analog¹¹ also reacted, but the yield was rather low (35%, run 3). The reaction of a methanesulfonamide-derived chloramine salt^{6a} with styrene gave a low yield of aziridine derivative **10** and the same result was obtained in one-pot synthesis which involved the *in situ* generation of the chloramine salt from methanesulfonamide, BuOCl and NaOH (29%, run 4).

Table 2. Aziridination of styrene using Chloramine-T derivatives.

Q R-S-N + Ö Na 1 mmol	Ph 2 mmol	l ₂ (10 MeCN / neutr rt,	nol%) ral buffer (1/1) 10 h	÷ N Ph	H 1: R = <i>p</i> -MeC ₆ H ₄ 8: R = Ph 9: R = <i>p</i> -NO ₂ C ₆ H ₄ 10: R = Me
	run	N source	product	yield / %	
	1	$R = p \text{-} MeC_6 H_4$	1	91	
	2	R = Ph	8	73	
	3	$R = p \text{-} NO_2 C_6 H_4$	9	35 ^a	
	4	R = Me	10	29	_
	a IH-NI	MR vield.			-

A variety of alkenes were examined with respect to this iodine-catalyzed aziridination using Chloramine-T under some selected conditions (Table 3). Method A was performed under the previously described conditions, which gave good results for the aziridination of styrene. The reaction using acetonitrile as a solvent (method B) proceeded more slowly than in the MeCN/neutral buffer (method A) for the aziridination of styrene and, as a result, the reaction time was extended to 24 h in method B. When 1,2-dihydronaphthalene was employed in the reaction using method A, a good yield of the corresponding aziridine was obtained (run 3). The present reaction was also found to be applicable to aliphatic olefins. 1-Octene was aziridinated in good yield using method B, rather than method A in contrast to the aziridination of styrene or 1,2-dihydronaphthalene (run 5, 6). When the amount of iodine was increased to 20 mol%, the yield of aziridine remained unchanged (run 7). Other acyclic and cyclic alkenes such as *trans*- and *cis*-2-octene, 2-methyl-2-heptene and cyclohexene showed a similar tendency (run 8-18). It is noteworthy that a high degree of stereospecificity was observed in the aziridination of *trans*- and *cis*-2-octene (run 8-12). However, the aziridine derived from trans- β -methylstyrene was obtained in 70% yield as a *cis/trans* mixture in method A (run 19). The yield of aziridine was increased by changing from method A to

method B, but the ratio of *cis/trans* isomers remained unchanged (run 20, 21). *Cis*- β -methylstyrene gave only the corresponding *cis*-aziridine but yield was low (run 22-24). Although the reason for why the stereoselectivity was low in the case of *trans*- β -methylstyrene is unclear, it is certain that the isomerization of aziridine did not occur in the present reaction because the *cis/trans* ratio was unaltered even when the reaction time was changed in the range of 3 to 24 h.

run	substrate	method ^a	cat. / mol%	yield (<i>cis:trans</i>) / % ^b
1	Ph	A	10	91
2		B	10	76
3	\bigcirc	A	10	65 ^c
4		B	20	38
5	C ₆ H ₁₃	A	20	52
6		B	10	66
7		B	20	67
8 9 10	Ме С ₅ Н ₁₁	A B B	20 10 20	40 ^d (<5 : >95) ^e 72 (<5 : >95) ^e 74 (<5 : >95) ^e
11	C ₅ H ₁₁ Me	B	10	61 (>95∶<5) ^e
12		B	20	63 (>95∶<5) ^e
13 14 15	Me C ₄ H ₉ Me	A B B	10 10 20	32 39 50
16	\bigcirc	A	10	56
17		B	10	74 d
18		B	20	72
19	Ph Me	A	20	70 ^d (38 : 62)
20		B	10	84 (30 : 70)
21		B	20	69 (30 : 70)
22	Ph Me	A	20	30 ^d (>95 : <5) ^e
23		B	10	16 ^d (>95 : <5) ^e
24		B	20	38 (94 : 6)

Table 3. Aziridination of alkenes using the I2-Chloramine-T system.

^a Conditions of method A; MeCN/neutral buffer, 10 h, rt. method B; MeCN, 24 h, rt. ^b Isolated yield based on Chloramine-T. *Cisltrans* ratios determined by ¹H-NMR integration are in parentheses. ^c 24 h. ^d ¹H-NMR yield based on Chloramine-T. ^e The minor isomer was not detected by ¹H-NMR in each case.

In order to better understand the most likely pathway for this reaction, the following experiments were attempted. We first checked whether iodine reacts with either an alkene or Chloramine-T by UV-vis spectroscopy. The UV-vis spectrum of a solution of iodine in acetonitrile/H₂O showed an absorption at 450 nm, and the subsequent addition of an equimolar amount of Chloramine-T caused a significant decrease in this peak,

13491

indicating that the reaction of Chloramine-T with iodine is very rapid. On the other hand, the reaction rate of styrene with iodine was smaller than that of Chloramine-T, as evidenced by UV-vis spectroscopy. The formation of iodohydrine $\mathbf{6}$ in the aziridination of styrene under the conditions where an equimolar amount of iodine was used suggests the possibility of the existence of an iodonium intermediate. It is known that the reaction of dichloramine-T or dibromamine-T with styrene gives the corresponding haloaminated compound.^{12,13} These facts support the generation of an iodoaminated compound in this system, although the compound would be so unstable that it could not be isolated. These conclusions assume that the reaction proceeds by the following mechanism (Scheme 1). Chloramine-T immediately reacts with iodine to form iodine-Chloramine-T complex 11. This complex then reacts with the alkene to give an iodonium cation intermediate 12. The iodoaminated intermediate 13 is formed by an attack of the nitrogen of Chloramine-T on the intermediate 12. Cyclization of compound 13 leads to the aziridine and the regeneration of 11. If this mechanism is correct, the aziridination proceeds with ICl instead of iodine. To examine this further, we carried out the aziridination of styrene by employing a catalytic amount of ICl, and the aziridine 1 was obtained in 64% yield. However, when Br₂ was used as a catalyst, the aziridination product was obtained in poor yield. This result is in good agreement with the fact that no cyclization products were obtained when dibromamine-T was added to alkenes.¹³ That is, the bromoaminated compound was not able to cyclize to the corresponding aziridine and regenerate the catalyst.



Scheme 1. Proposed mechanism of the aziridination of alkenes.

CONCLUSION

In conclusion, we have developed a simple and efficient method for the aziridination of various alkenes utilizing Chloramine-T and a catalytic amount of iodine. The aziridination of both conjugated alkenes with an aryl group and non-conjugated compounds proceeded with good yields, by altering the solvent or the amount of iodine. It was also found an electron-releasing para-substituent on styrene accelerated the aziridination of the substituted styrene derivatives. Interestingly the stereospecific aziridination was observed in the reactions of *cis*- and *trans*- β -methylstyrene. Although some Chloramine-T analogs could be used in the present reaction, the corresponding aziridines were obtained in moderate yields. The mechanism of this reaction is presently unclear, but auxiliary experiments suggest the generation of an iodine-

Chloramine-T complex and an iodonium cation intermediate. Further investigations on the reaction mechanism are now in progress.

EXPERIMENTAL

General. Melting points were determined on a Yanagimoto micro melting point apparatus and are uncorrected. IR spectra were obtained on a Hitachi 270-30 infrared spectrophotometer. ¹H and ¹³C-NMR spectra were recorded on a JEOL FT-NMR JNM EX 270 spectrometer (¹H-NMR, 270 MHz; ¹³C-NMR, 68 MHz) using tetramethylsilane as an internal standard. Mass spectra were measured on Shimadzu Model GCMS-QP5000 spectrometer. High-resolution mass spectral data were obtained on a JEOL DX-303 mass spectrometer. Flash column chromatography (FCC) was performed using silica gel BW-300 (Fuji Silysia Chemical Co.). Preparative gel permeation liquid chromatography (GPLC) was performed on a JAI (Japan Analytical Industry) LC-908 instrument with JAIGEL 1H-2H columns and chloroform as an eluent. UV-vis spectra with a Shimadzu UV-265 spectrophotometer equipped with Shimadzu TCC-260 thermostated cell holder. Analytical thin layer chromatography was performed using EM reagent 0.25 mm silica gel 60-F plates. Visualization was accomplished with UV light and phosphomolybdic acid ethanol solution followed by heating. All reactions were carried out under a nitrogen atmosphere, unless otherwise noted. Organic solvents were dried and distilled prior to use.

General Procedure for Preparation of Aziridines.

Method A. The alkenes (2.0 mmol) were added to a solution of iodine (0.1 mmol, 10 mol%), Chloramine-T (1.0 mmol), and naphthalene (ca. 0.5 mmol; internal standard) in acetonitrile/buffer solution (1.5 mL/1.5 mL). The solution was allowed to stir at room temperature under a nitrogen atmosphere. The rate of formation of aziridines was monitored by HPLC [pump: Hitachi L-600; UV-detector: Hitachi 638-0430 UV monitor; column: Kanto Mightysil RP-18 GP, eluent: MeOH/H₂O, 7:3]. After the addition of CH₂Cl₂ (40 mL) and water (20 mL), the phases were separated and the aqueous phase was extracted with CH₂Cl₂ (20 mL). The combined organic extracts were washed with water (20 mL x 3) and brine (20 mL), dried over K₂CO₃ and concentrated to give the crude product. Purification by flash column chromatography (silica gel, 20% ethyl acetate in hexane) gave the aziridines as a white crystalline solid or colorless oil.

Method B. Acetonitrile/buffer solvent (1.5 mL/1.5 mL) of method A was changed to acetonitrile (3 mL)

2-[*N*-(*p*-Toluenesulfonyl)amino]-1-phenylethanol (7); white crystalline solid; mp. 107-108 °C; TLC R_f 0.40 (hexane:EtOAc = 1:1); IR (KBr, cm⁻¹) 3420 (NH), 1316, 1142 (SO₂); ¹H NMR (CDCl₃, 270 MHz) δ 7.73 (d, 2H, *J* = 8.6 Hz, ArH), 7.37-7.27 (m, 7H, ArH), 4.96 (dd, 1H, *J* = 7.8, 4.3 Hz, TsNH), 4.80 (ddd, 1H, *J* = 8.6, 3.8, 3.8 Hz, PhCHOH), 3.25 (ddd, 1H, *J* = 13.2, 7.8, 3.8 Hz, TsNHCH₂), 3.03 (ddd, 1H, *J* = 13.2, 8.7, 4.3 Hz, TsNHCH₂), 2.44 (d, 1H, *J* = 3.8 Hz, OH), 2.42 (s, 3H, Ar-CH₃); ¹³C NMR (CDCl₃, 68 MHz) δ 143.6, 140.7, 136.5, 129.8, 128.6, 128.2, 127.0, 125.8, 72.6, 50.1, 21.5; MS (CI, methane) 292 (M⁺+1); HRMS (CI, methane) exact mass calcd for C₁₅H₁₇NO₃S (M + H)⁺ 292.1007, found 292.1008. Anal. Calcd for C₁₅H₁₇NO₃S: C, 61.83; H, 5.88; N, 4.81. Found: C, 61.56; H, 5.77; N, 4.75.

N-(Benzenesulfonyl)-2-phenylaziridine (8); white crystalline solid; TLC R_f 0.33 (hexane:EtOAc = 1:1); mp 70-72 °C; IR (KBr, cm⁻¹) 1314, 1152 (SO₂); ¹H NMR (CDCl₃, 270 MHz) δ 7.98 (d, 2H, J = 7.6 Hz, ArH), 7.61 (t, 1H, J = 7.6 Hz, ArH), 7.52 (t, 2H, J = 7.6 Hz, ArH), 7.29-7.18 (m, 5H, ArH), 3.80 (dd, 1H, J = 7.0, 4.6 Hz, CHPh), 3.00 (d, 1H, J = 7.0 Hz, CHCH₂), 2.40 (d, 1H, J = 4.6 Hz, CHCH₂); ¹³C NMR (CDCl₃, 68 MHz) 137.9, 134.8, 133.6, 129.0, 128.5, 128.3, 127.8, 126.5, 41.0, 35.9; MS (CI, isobutane) 260 (M⁺+1); HRMS (CI, methane) exact mass calcd for C₁₄H₁₃NO₂S (M + H)⁺ 260.0745, found 260.0756. Anal. Calcd for C₁₄H₁₃NO₂S: C, 64.84; H, 5.05; N, 5.40. Found: C, 64.69; H, 5.06; N, 5.37.

N-(Methanesulfonyl)-2-phenylaziridine (10); colorless oil; TLC R_f 0.12 (hexane:EtOAc = 1:1); IR (neat, cm⁻¹) 1324, 1160 (SO₂); ¹H NMR (CDCl₃, 270 MHz) δ 7.38-7.29 (m, 5H, ArH), 3.72 (dd, 1H, J = 7.3, 4.6 Hz, CHPh), 3.11 (s, 3H, CH₃), 2.98 (d, 1H, J = 7.3 Hz, CHCH₂), 2.44 (d, 1H, J = 4.6 Hz, CHCH₂); ¹³C NMR (CDCl₃, 68 MHz) δ 134.8, 128.6, 128.4, 126.4, 40.6, 39.6, 35.3; MS (CI, methane) 198 (M⁺+1); HRMS (CI, methane) exact mass calcd for C₉H₁₁NO₂S (M + H)⁺ 198.0588, found 198.0583.

trans-N-(p-Toluenesulfonyl)-2-methyl-3-pentylaziridine; colorless oil; TLC R_f 0.43 (hexane:EtOAc = 1:1); IR (neat, cm⁻¹) 1306, 1148 (SO₂); ¹H NMR (CDCl₃, 270 MHz) δ 7.83 (d, 2H, J = 8.4 Hz, ArH), 7.31 (d, 2H, J = 8.4 Hz, ArH), 2.68 (m, 2H, CH-aziridine), 2.43 (s, 3H, Ar-CH₃), 1.60-1.54 (m, 5H, CH₂C₄H₉ and CHCH₃), 1.26-1.20 (m, 6H, CHCH₂CH₂CH₂CH₃), 0.83 (t, 3H, J = 6.3 Hz, CH₂CH₃); ¹3C NMR (CDCl₃, 68 MHz) δ 143.7, 138.1, 129.4, 127.3, 49.7, 45.9, 31.2, 30.4, 26.8, 22.4, 21.5, 14.7, 13.8; MS (CI, methane) 282 (M⁺+1); Anal. Calcd for C₁₅H₂₃NO₂S: C, 64.02; H, 8.24; N, 4.98. Found: C, 63.65; H, 8.15; N, 5.07.

cis-N-(p-Toluenesulfonyl)-2-methyl-3-pentylaziridine; colorless oil; TLC R_f 0.42 (hexane:EtOAc = 1:1); IR (neat, cm⁻¹) 1320, 1150 (SO₂); ¹H NMR (CDCl₃, 270 MHz) δ 7.82 (d, 2H, J = 8.3 Hz, ArH), 7.32 (d, 2H, J = 8.3 Hz, ArH), 2.92 (dq, 1H, J = 6.3, 5.0 Hz, CH-aziridine), 2.72 (dt, 1H, J = 6.3, 7.3 Hz, CH-aziridine), 2.44 (s, 3H, Ar-CH₃), 1.44-1.34 (m, 2H, CH₂C₄H₉), 1.21-1.19 (m, 9H, CHCH₂CH₂CH₂CH₃ and CHCH₃), 0.82 (t, 3H, J = 6.4 Hz, CH₂CH₃); ¹³C NMR (CDCl₃, 68 MHz) δ 144.1, 135.6, 129.5, 127.8, 45.2, 40.1, 31.3, 26.7, 26.3, 22.4, 21.5, 13.8, 12.0; MS (CI, methane) 282 (M⁺+1); Anal. Calcd for C₁₅H₂₃NO₂S: C, 64.02; H, 8.24; N, 4.98. Found: C, 63.83; H, 8.24; N, 5.10.

N-(*p*-Toluenesulfonyl)-2,2-dimethyl-3-butylaziridine; colorless crystalline solid; mp. 61-63 °C; TLC R_f 0.44 (hexane:EtOAc = 1:1); IR (KBr, cm⁻¹) 1306, 1142 (SO₂); ¹H NMR (CDCl₃, 270 MHz) δ 7.82 (d, 2H, J = 8.1 Hz, ArH), 7.30 (d, 2H, J = 8.1 Hz, ArH), 2.84 (dd, 1H, J = 7.6, 5.9 Hz, CH-aziridine), 2.43 (s, 3H, Ar-CH₃), 1.71 (s, 3H, CH₃-aziridine), 1.41-1.13 (m, 9H, CH₂CH₂CH₂CH₃ and CH₃-aziridine), 0.79 (t, 3H, J = 7.1 Hz, CH₂CH₃); ¹³C NMR (CDCl₃, 68 MHz) δ 143.5, 138.4, 129.3, 127.3, 52.8, 51.8, 29.4, 27.4, 22.2, 21.5, 21.4, 21.2, 13.8; MS (CI, isobutane) 282 (M⁺+1); Anal. Calcd for C₁₅H₂₃NO₂S: C, 64.02; H, 8.24; N, 4.98. Found: C, 63.74; H, 8.14; N, 5.03.

UV-vis analysis. The reactions of iodine with Chloramine-T or styrene were followed by the UV-vis spectrophotometry in MeCN/H₂O at 30 °C. Typically, a MeCN/H₂O solution of iodine (1 mM) was placed in a UV cell (1 cm path length) and a MeCN/H₂O solution of Chloramine-T (1 mM) was added to initiate the reaction.

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