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A CONVENIENT SYNTHESIS OF NEW 1-ALKYNYL-1*H*-BENZOTRIAZOLES BY REACTION OF ALKYNYL(PHENYL)IODONIUM SALTS WITH BENZOTRIAZOLE ION

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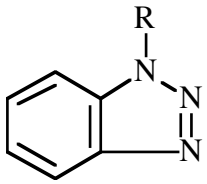
Abstract- The reaction of arylethynyl(phenyl)iodonium tosylates with benzotriazole ion gave new 1-alkynyl-1*H*-benzotriazoles in good yields. This result indicates that alkynyliodonium salts can be used for direct alkynylation of benzotriazole. However, the similar reactions of (*tert*-butylethynyl)(phenyl)iodonium and 1-octynyl(phenyl)iodonium tosylates do not afford the 1-alkynyl-1*H*-benzotriazoles but alkenylbenzotriazoles *via* the reaction of alkylidenecarbenes.

Much attention has been paid to 1*H*-benzotriazoles (**1**) in recent years because of their increasing use in organic chemistry, biochemistry and industry.[1] The synthesis of the functionalized 1*H*-benzotriazoles (**1**) is considered to become important subjects of synthetic and biological researches since they are expected to exhibit novel properties applicable to such fields. In the light of recent development of acetylene chemistry[2] ranging over material science and biochemistry as well as organic chemistry, where the acetylenic bond plays a significant role in the reactions and applications, the combination of the acetylenic bond and the benzotriazole functionality is thought to create a new chemistry. Although 1-alkenyl-1*H*-benzotriazoles (**2**) have been prepared by several methods,[3] to the best of our knowledge, there are no reports on 1-alkynyl-1*H*-benzotriazoles (**3**).

Direct alkynylation is a simple and convenient method for the preparation of alkynyl derivatives. However, the direct introduction of a carbon-carbon triple bond on the nitrogen atom of benzotriazole seems to be difficult. Alkynylation using alkynyl cations is not practical in the most cases because alkynyl cations are unstable and impossible to be generated except for nuclear decay of a tritiated alkyne.[4]

This paper is dedicated to Professor Teruaki Mukaiyama on the occasion of his 73rd birthday.

On the other hand, hypervalent iodine chemistry has been much studied recently and increased the utility of hypervalent iodine compounds in organic synthesis.[5] Above all, alkynyl(phenyl)iodonium saltshave beenrecognizedtobeusefulassynthonofalkynylcations.[6]Thusweselectedalkynyl(phenyl)iodonium tosylates(**4**)asthesubstrateforthealkynylationreactionofbenzotriazoleandconducted the reaction of alkynyliodonium salts (**4**) with benzotriazole. In the previous paper,[7] we have preliminarily reported that alkynyl(phenyl)iodonium salts (**4**) act as an alkynylating agent for benzotriazole and provided 1-alkynylbenzotriazoles (**3**) in the reaction with benzotriazole ion. In this paper, we describe in detail the reaction of alkynyl(phenyl)iodonium tosylates (**4**) with benzotriazole ion, and discuss the scope of this method with respect to the 1-alkynylbenzotriazole synthesis.



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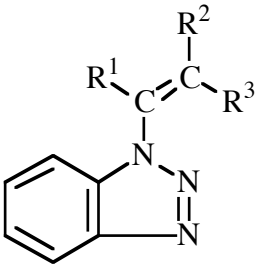

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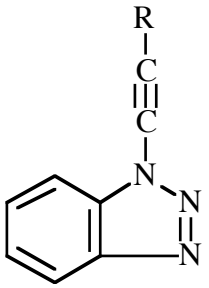

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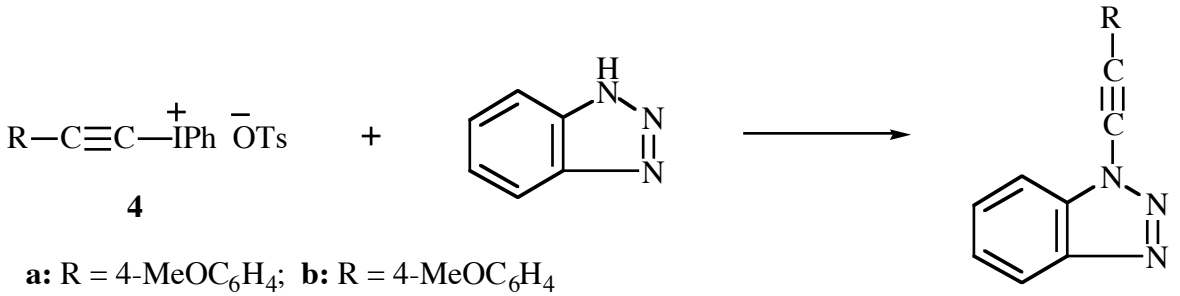


4

a: R = 4-$MeOC_6H_4$; **b:** R = 4-$MeOC_6H_4$
c: R = Ph; **d:** R = 4-ClC_6H_4
e: R = *tert*-Bu; **f:** R = *n*-C_6H_{13}

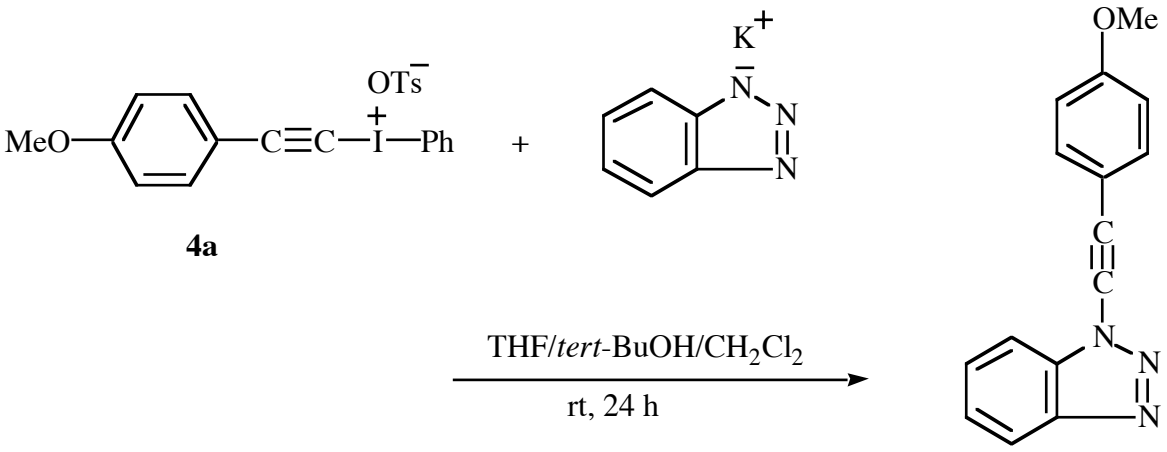
3

RESULTS AND DISCUSSION

Alkynyl(phenyl)iodonium tosylates (**4:** X = OTs) were prepared by the reaction of terminal alkynes with hydroxy(tosyloxy)iodobenzene according to the methods described in the literature.[8,9] The preparation of 1-hexynyl(phenyl)iodonium tosylate (**4f:** R = *n*-C_6H_{13}, X = OTs) was conducted by the reaction of 1-trimethylsilyl-1-octyne with iodosylbenzene.[10]

First we studied the reaction of [(4-methoxyphenyl)ethynyl](phenyl)iodonium tosylate (**4a**) with benzotriazole ion. A solution of potassium salt of benzotriazole was prepared from *tert*-BuOK and benzotriazole in a mixed solvent of *tert*-BuOH and THF, then solid alkynyliodonium tosylate (**4a**) was added into the solution, and the reaction mixture was stirred for 12 h. However, it was found that this procedure gave 1-[(4-methoxyphenyl)ethynyl]-1*H*-benzotriazole (**3a**) in a low yield (29%). Then, we changed the order of the addition of the reagents. The THF and *tert*-BuOH solution of potassium salt of benzotriazole prepared above was added to a solution of alkynyliodonium tosylate (**3a**) in a mixed solvent

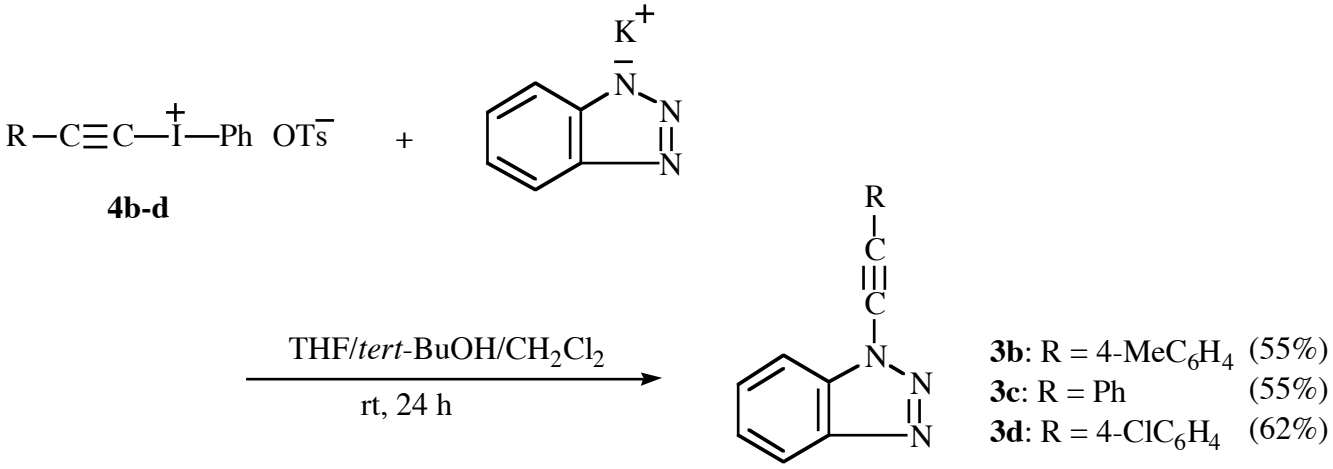
of *tert*-BuOH and CH_2Cl_2 and the mixture was stirred at rt for 24 h. This operation using the reverse addition much improved the yield of alkynylbenzotriazole (**3a**) (58% yield).



4a **3a**

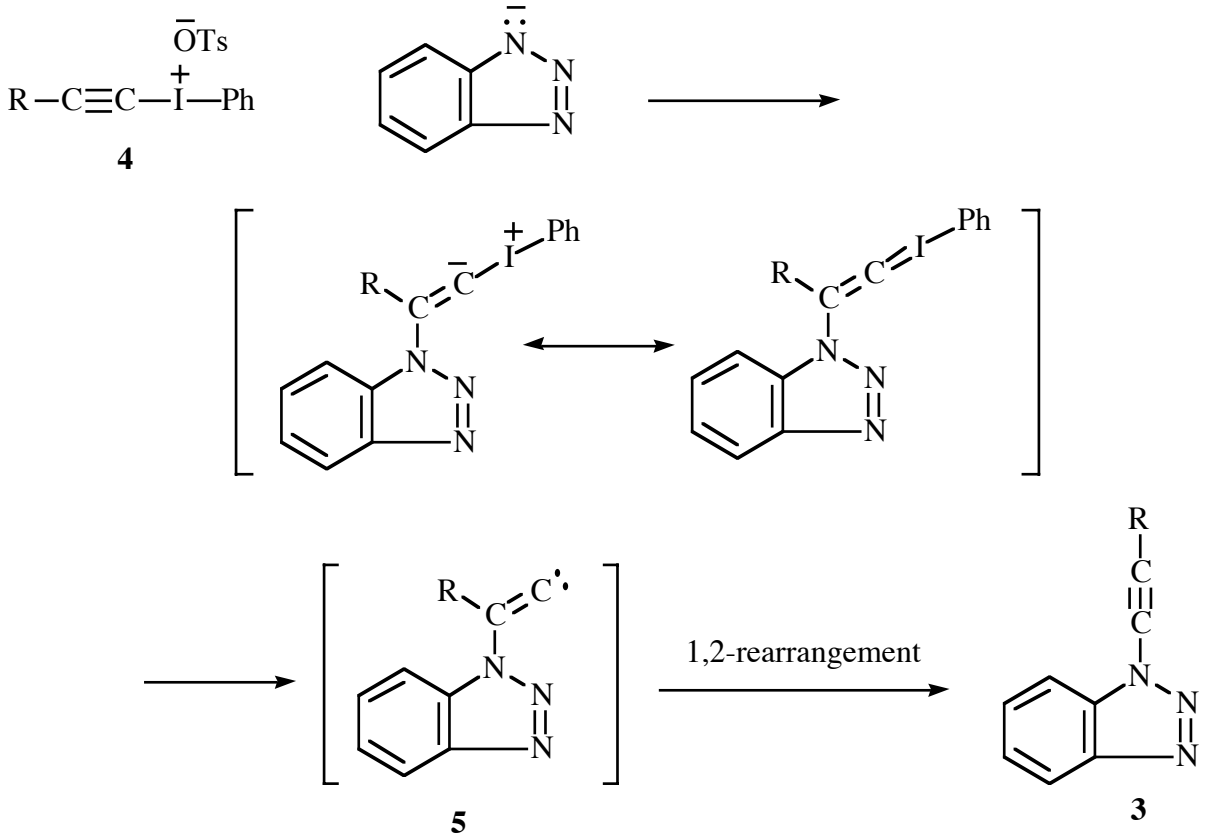
To optimize the yield of 1-alkynyl-1*H*-benzotriazole (**3a**), we examined several solvent systems. Methanol and MeCN-H_2O solvents gave the moderate yields (27 and 20 %, respectively) of **3a**. The following solvent systems afforded better results: CH_2Cl_2 (50%), *tert*-BuOH-CH_2Cl_2 (56%), and *tert*-BuOH-H_2O (50%).

Similar treatment of other alkynyl(phenyl)iodonium tosylates (**4b-d**) gave the corresponding 1-alkynyl-1*H*-benzotriazoles (**3b-d**) as crystals in 45-62% yields.



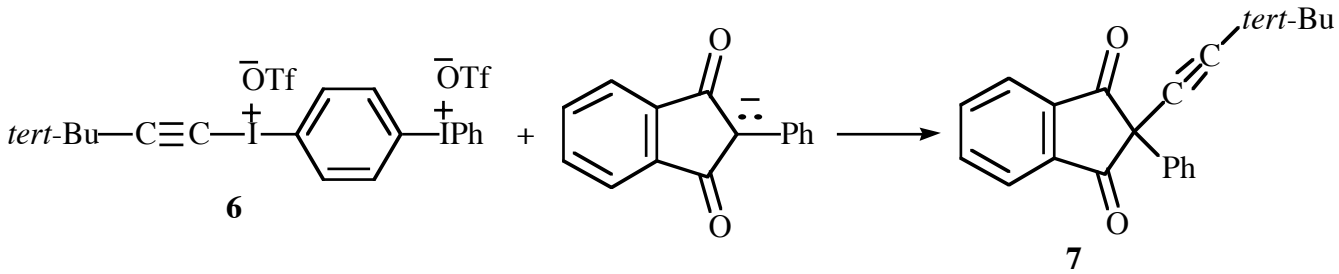
4b-d

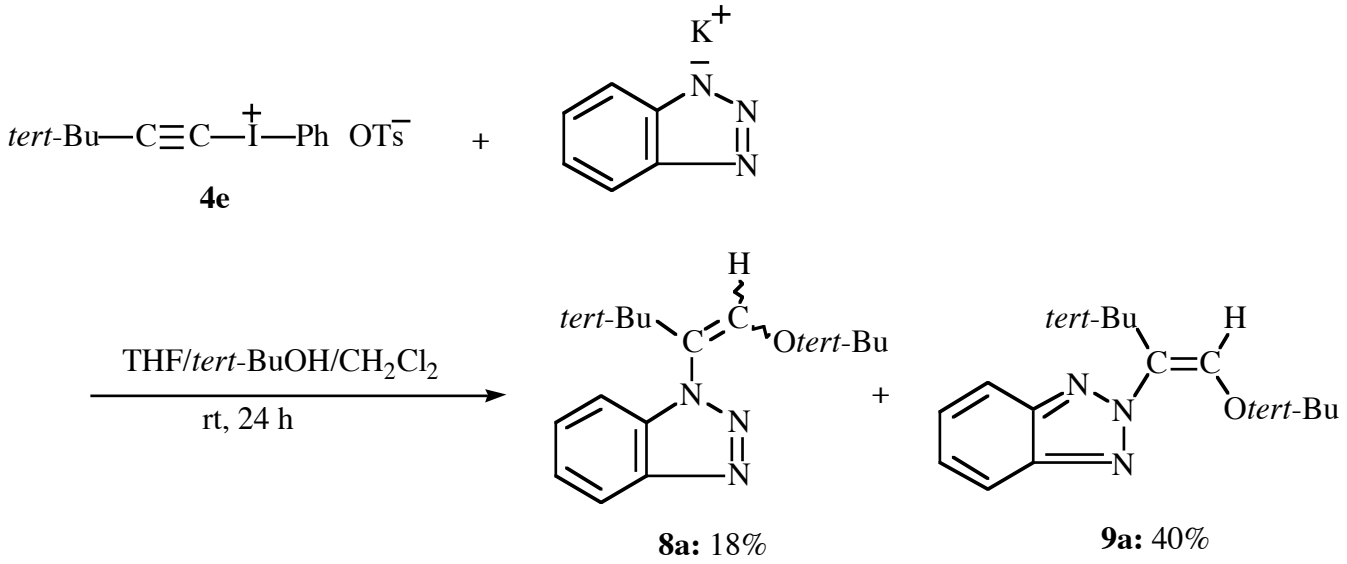
The formation of 1-alkynyl-1*H*-benzotriazoles (**3**) indicates that alkynyliodonium salts (**4**) behave as the alkynylating agent of benzotriazole and are regarded as the synthon of alkynyl cations. However, the present reaction is reasonably considered to proceed *via* the Michael addition of benzotriazole ion to the β carbon of the triple bond, the formation of alkylidenecarbenes (**5**), and finally the rearrangement to the alkynylbenzotriazole (**3**), as it has been well recognized in the reaction of alkynyliodonium salts.[6]



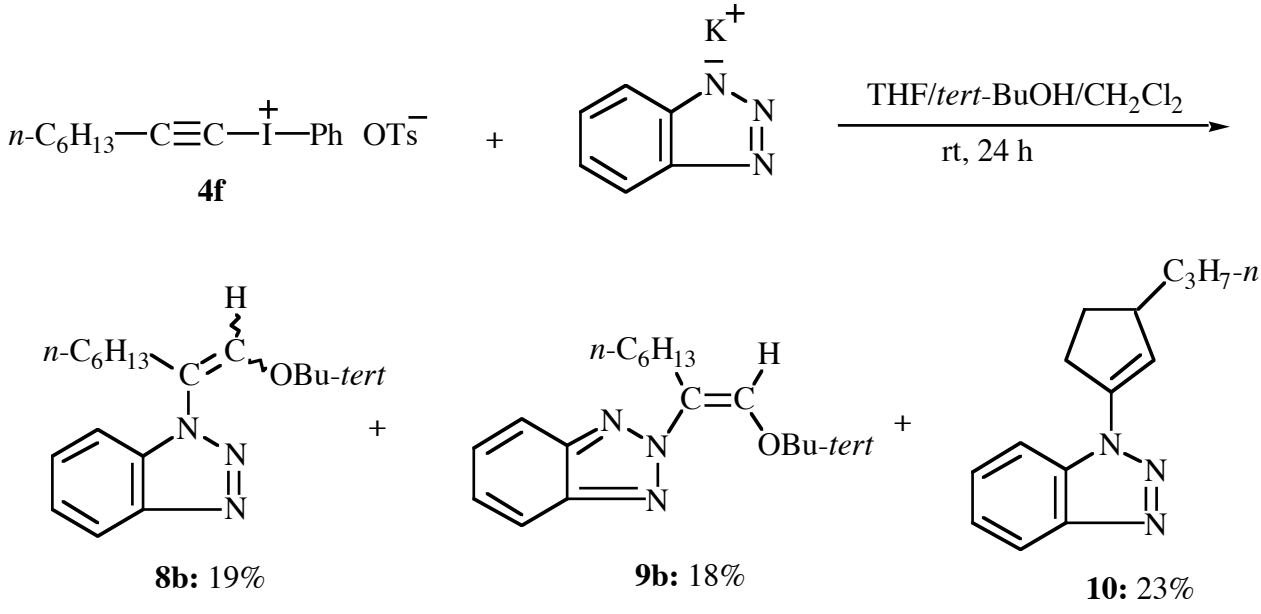
Scheme 1

In order to examine the scope and limitation on the present reaction, we conducted the reaction of (*tert*-butylethynyl)(phenyl)iodonium tosylate (**4e**) with benzotriazole ion. However, the reaction of **4e** with benzotriazole ion did not yield 1-(*tert*-butylethynyl)-1*H*-benzotriazole (**3e**), but a mixture of (*E*)- and (*Z*)-(*E*)-1-vinyl-1*H*-benzotriazoles (**8a**) in 18% yield, along with (*Z*)-2-vinyl-2*H*-benzotriazole (**9a**) in 40% yield. In our previous report[11] on the reaction of (*tert*-butylethynyl)(*p*-phenylene)bisiodonium ditriflate (**6**) with the enolate anion of 2-phenyl-1,3-indandione, 3-(*tert*-butylethynyl)-2-phenyl-1,3-indandione (**7**) has been obtained as the sole product. In the reaction with the enolate anion of 2-phenyl-1,3-indandione, 1,2-rearrangement has been observed and no *tert*-butanol-incorporated products have been detected. Therefore, these results indicate that the benzotriazolyl group retards the 1,2-rearrangement and enables the reaction with *tert*-butanol.



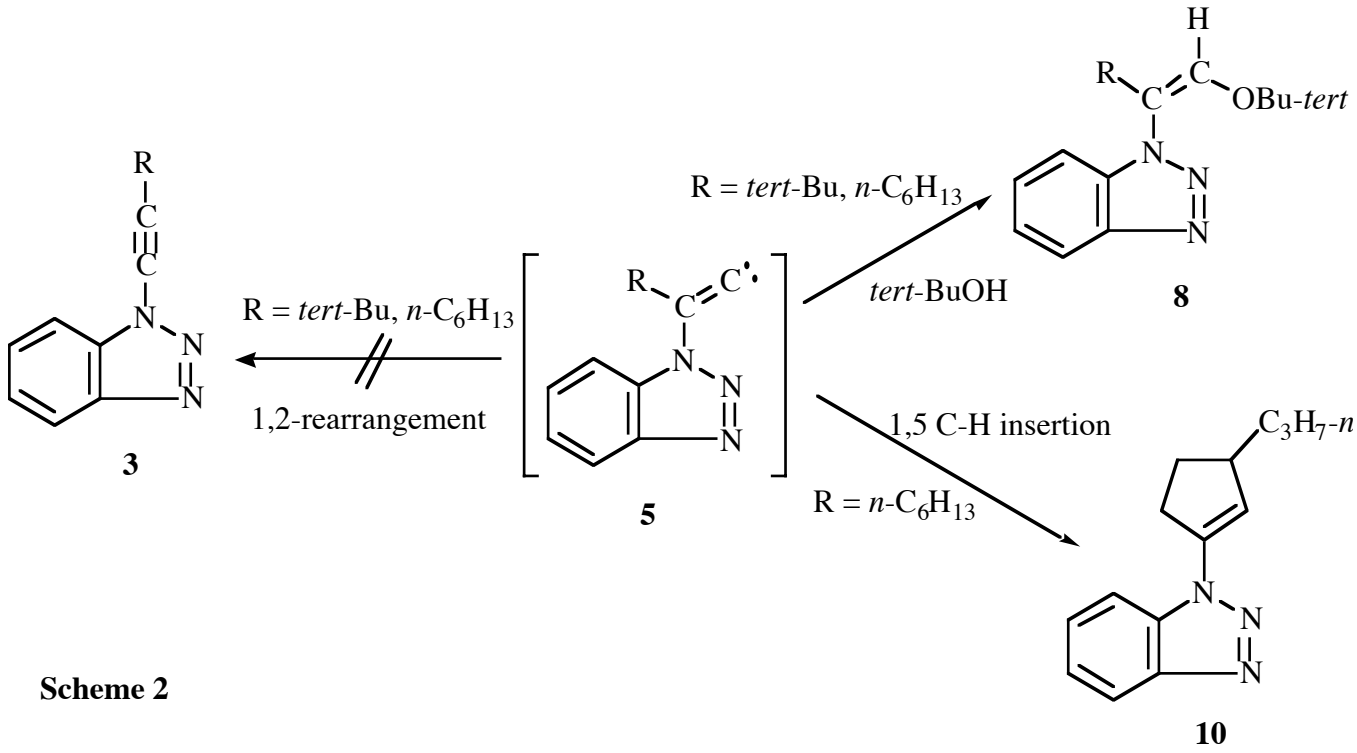


Similarly, the reaction of 1-octynyl(phenyl)iodonium tosylate (**4f**) with benzotriazole ion afforded a mixture of (*E*)- and (*Z*)-1-vinyl-1*H*-benzotriazoles (**8b**), (*Z*)-2-vinyl-2*H*-benzotriazole (**9b**), and 1-(3-propyl-1-cyclopentenyl)-1*H*-benzotriazole (**10**) in 19, 18, and 23% yields, respectively. The formation of **10** strongly suggests the intervention of alkylidenecarbene (**5**) that undergoes 1,5 C-H insertion reaction as the typical reaction.[12]



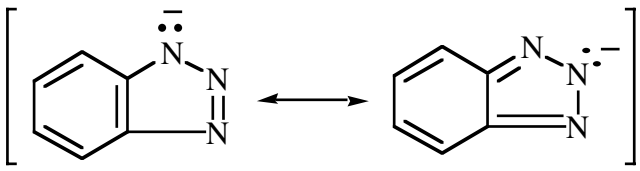
The results obtained above indicates that alkyl-substituted ethynyliodonium tosylates (**4e** and **f**) do not give 1-alkynylbenzotriazoles (**3e** and **f**) in the reaction with benzotriazole ion. This fact is attributableto the nature of the migrating substituents. In general, the migration of alkyl groups is much slowerthanthat of aryl groups.[13] The benzotriazolyl group is considered to show a very low migratory aptitude in this kind of reaction since the general migratory aptitude of carbenes indicates the following trend: RS > H > Ph > alkyl > RO > R_2N,[13] that is, nitrogen substituents migrate slower than aryl and alkyl groups. The same result on the rearrangement has been observed in the reaction with azide ion where no 1,2-

rearrangement occurs.[14] Therefore, it is concluded that the reaction of **1** with benzotriazole ion proceeds *via* alkylidenecarbene (**5**) which undergoes a typical intramolecular 1,5 C–H insertion to cyclopropenylbenzotriazole (**10**) and/or an electrophilic attack toward *tert*-BuOH giving **8**, as shown in Scheme 2.



Scheme 2

Furthermore, the formation of 2-vinyl-2*H*-benzotriazoles (**9**) suggests that benzotriazole ion acts as an ambident nucleophile. Such behavior of benzotriazole ion has been observed in the isomerization of aminomethylbenzotriazoles that occurs with a dissociative pathway to the iminium ion and benzotriazole ion and the subsequent recombination.[15]



In summary, we have for the first time synthesized new 1-alkynylbenzotriazoles (**3**) by use of alkynyliodonium salts (**1**) and benzotriazole ion. The utility of alkynylation reaction using alkynyliodonium salts (**1**) has been further advanced. The useful functionality of the alkynyl and benzotriazole groups will be developed in the near future.

EXPERIMENTAL

Melting points were determined with a Yanaco melting point apparatus and are uncorrected. ^{1}H NMR spectra were taken with Buruker AC-250 (250 MHz) and JEOL JNM-AL300 (300 MHz) and ^{13}C NMR spectra were with Bruker AC-250 (63 MHz) and JEOL AL300 (75 MHz) spectrometers. IR spectra were recorded on a HORIBA FT-200 spectrophotometer. Elemental analyses were performed by the Service Center of the Elementary Analysis of Organic Compounds, Faculty of Science, Kyushu University.

GENERAL PROCEDURE FOR PREPARATION OF 1-ALKYNYL-1*H*-BENZOTRIAZOLES

To a solution of *tert*-BuOK (0.123 g, 1.1 mmol) in *tert*-BuOH (10 mL) was added a solution of benzotriazole (0.131 g, 1.1 mmol) in THF (10 mL). After the mixture was stirred at rt for 1 h, the solution of potassium salt of benzotriazole was added to a solution of an alkynyl(phenyl)iodonium tosylate (1.0 mmol) in a mixed solvent of *tert*-BuOH (10 mL) and CH_2Cl_2 (10 mL) and the mixture was stirred for 24 h. The reaction mixture was poured into water and the product was extracted with ether. The ethereal extract was washed with water and brine, and dried over anhydrous Na_2SO_4. After evaporation of the solvent, the product was separated by a preparative thin-layer chromatography with hexane and CH_2Cl_2 as eluents. The products were further purified by recrystallization from CH_2Cl_2 and hexane.

1-[4-(Methoxyphenyl)ethynyl]benzotriazole (3a): mp 98.5-100.6 ˚C; ^{1}H-NMR (250 MHz,$CDCl_3$)δ 3.71 (s, CH_3, 3H), 6.79 (d, *J* = 7.8 Hz, ArH, 2H), 7.33 (d, *J* = 7.5 Hz, ArH, 1H), 7.42-7.51 (m, ArH, 3H), 7.58 (d, *J* = 8.0 Hz, ArH, 1H), 7.97 (d, *J* = 8.2 Hz, ArH, 1H); ^{13}C-NMR (63 MHz, $CDCl_3$) δ 54.32, 74.86, 79.91, 110.13, 112.48, 114.22, 120.55, 125.15, 129.22, 133.65, 134.38, 143.98, 160.72; IR (KBr) 2246 cm^{-1} (C≡C). Anal. Calcd for $C_{15}H_{11}N_3O$: C, 72.28; H, 4.45; N, 16.86. Found:C,72.15;H, 4.45; N, 16.87.

1-[4-(Methylphenyl)ethynyl]benzotriazole (3b): mp 81.7-84.6 ˚C; ^{1}H-NMR (250 MHz, $CDCl_3$) δ 2.39 (s, CH_3, 3H), 7.21 (d, *J* = 7.8 Hz, ArH, 2H), 7.42-7.64 (m, ArH, 4H), 7.73 (d, *J* = 8.2 Hz, ArH, 1H), 8.11 (d, *J* = 8.3 Hz, ArH, 1H); ^{13}C-NMR (63 MHz, $CDCl_3$) δ 21.44, 75.20, 79.84, 110.75, 117.39, 120.22, 125.16, 129.28, 131.74, 131.80, 134.16, 139.82, 143.81; IR (KBr) 2244 cm^{-1} (C≡C). Anal. Calcd for $C_{15}H_{11}N_3$: C, 77.23; H, 4.75; N, 18.01. Found: C,76.96;H, 4.85; N, 17.97.

1-(Phenylethynyl)benzotriazole (3c): mp 76.5-77.5 ˚C; ^{1}H-NMR (250 MHz, $CDCl_3$) δ 7.36-7.44(m, ArH, 4H), 7.55-7.67 (m, ArH, 4H), 8.05 (d, *J* = 8.3 Hz, ArH, 1H); ^{13}C-NMR (63 MHz, $CDCl_3$) δ 75.48, 79.46, 109.63, 120.19, 124.94, 128.25, 130.20, 131.49, 133.77, 143.47; IR (KBr) 2259 cm^{-1} (C≡C). Anal. Calcd for $C_{15}H_9N_3$: C, 76.70; H, 4.14; N, 19.17. Found: C, 76.49; H, 4.15; N, 19.17.

1-[4-(Chlorophenyl)ethynyl]benzotriazole (3d): mp 147.2-147.9 ˚C; ^{1}H-NMR (250 MHz, $CDCl_3$)δ 7.44-7.67 (m, ArH, 5H), 7.72 (d, *J* = 6.8 Hz, ArH, 1H), 7.79 (d, *J* = 7.8 Hz, ArH, 1H), 8.19 (d, *J* = 8.2 Hz, ArH, 1H); ^{13}C-NMR (63 MHz, $CDCl_3$) δ 78.71, 110.13, 119.06, 120.36, 120.70, 125.28, 128.92, 129.31, 133.02, 134.05, 135.58, 143.82; IR (KBr) 2261 cm^{-1} (C≡C). Anal. Calcd for $C_{14}H_8N_3Cl$: C, 66.28; H, 3.18; N, 16.56. Found: C, 66.00; H, 3.25; N, 16.51.

REACTION OF (*tert*-BUTYLETHYNYL)(PHENYL)IODONIUM TOSYLATE (4e) WITH BENZOTRIAZOLE ION

A solution of *tert*-BuOK (0.673 g, 6.0 mmol) and benzotriazole (0.714 g, 6.0 mmol) in *tert*-BuOH (50 mL) and THF (10 mL) was stirred at rt for 1 h. The resulting solution of potassium salt ofbenzotriazole was added to a solution of (*tert*-butylethynyl)(phenyl)iodonium tosylate (**4e**) (5.0 mmol) in a mixed solvent of *tert*-BuOH (20 mL) and CH_2Cl_2 (20 mL) at 0 ˚C and the mixture was stirred at rt for 24 h. The reaction mixture was poured into water and the product was extracted with CH_2Cl_2. The CH_2Cl_2extract was washed with water and brine, and dried over anhydrous Na_2SO_4. After evaporation of the solvent, the product was separated by column chromatography on silica gel with hexane and CH_2Cl_2 as eluents. A mixture of (*E*)- and (*Z*)-**8a** was further separated by a recycling preparative HPLC equipped with a GPC column. The (*Z*) configuration of **8a** and **9a** was determined by the observation of NOE between the *tert*-Bu and vinylic protons.

1-[(*E*)-3,3-Dimethyl-1-(2-methyl-2-propoxy)-1-buten-2-yl]-1*H*-benzotriazole (8a): mp 80-85 ˚C (CH_2Cl_2-hexane); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.19 (s, *tert*-Bu, 9H), 1.35 (s, *tert*-Bu, 9H), 6.52 (s, =CH, 1H), 7.34-7.38 (m, ArH, 1H), 7.45-7.50 (m, ArH, 2H), 8.05 (d, *J* = 9.0 Hz, ArH, 1H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 27.82, 28.62, 35.54, 78.40, 110.26, 119.58, 123.46, 124.03, 127.44, 135.89, 142.61. The (*E*) isomer could not be purified completely because of some impurities.

1-[(*Z*)-3,3-Dimethyl-1-(2-methyl-2-propoxy)-1-buten-2-yl]-1*H*-benzotriazole (8a): mp 107-108 ˚C (CH_2Cl_2-hexane); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.11 (s, *tert*-Bu, 9H), 1.20 (s, *tert*-Bu, 9H), 6.74 (s, =CH, 1H), 7.29-7.45 (m, ArH, 3H), 8.05 (d, *J* = 8.4 Hz, ArH, 1H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 27.68, 29.06, 35.08, 77.50, 110.83, 119.35, 123.06, 123.91, 126.70, 134.70, 137.29, 144.82. Anal. Calcd for $C_{16}H_{23}N_3O$: C, 70.30; H, 8.48; N, 15.37. Found: C, 70.29; H, 8.51; N, 15.46.

2-[(*Z*)-3,3-Dimethyl-1-(2-methyl-2-propoxy)-1-buten-2-yl]-2*H*-benzotriazole (9a): mp 94-95 ˚C (CH_2Cl_2-hexane); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.17 (s, *tert*-Bu, 9H), 1.21 (s, *tert*-Bu, 9H), 6.68 (s, =CH, 1H), 7.30-7.34 (m, ArH, 2H), 7.91-7.94 (m, ArH, 2H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 27.31, 28.65, 34.28, 77.32, 117.88, 125.40, 130.59, 137.12, 143.58. Anal. Calcd for $C_{16}H_{23}N_3O$: C, 70.30;H, 8.48; N, 15.37. Found: C, 70.29; H, 8.45; N, 15.35.

REACTION OF (1-OCTYNYL)(PHENYL)IODONIUM TOSYLATE (4f) WITH BENZOTRIAZOLE ION

A solution of *tert*-BuOK (0.123 g, 1.1 mmol) and benzotriazole (0.131 g, 1.1 mmol) in *tert*-BuOH (25 mL) and CH_2Cl_2 (5 mL) was stirred at rt for 1 h. The resulting solution of potassium salt of benzotriazole was added dropwise to a solution of (1-octynyl)(phenyl)iodonium tosylate (**4f**) (1.0 mmol) in CH_2Cl_2 (30 mL) at 0 ˚C and the mixture was stirred at rt for 24 h. The reaction mixture was poured into water and the product was extracted with CH_2Cl_2. The CH_2Cl_2-extract was washed with water and brine, and dried over anhydrous Na_2SO_4. After evaporation of the solvent, the product wasseparatedby column chromatography on silica gel with hexane and CH_2Cl_2 as eluents.

1-[(*E*)-1-(2-Methyl-2-propoxy)-1-octen-2-yl]-1*H*-benzotriazole (8b): Oil; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 0.83 (t, *J* = 7 Hz, Me, 3H), 1.22-1.37 (m, $(CH_2)_4$ and *tert*-Bu, 17H), 2.72 (t, *J* = 7 Hz, CH_2, 2H), 6.79 (s, =CH, 1H), 7.34-7.49 (m, ArH, 3H), 8.06 (d, *J* = 8 Hz, ArH, 1H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 13.99, 22.52, 26.60, 27.77, 28.05, 28.47, 31.37, 78.05, 110.10, 119.91, 123.71, 124.79, 127.29, 134.15, 140.44, 145.60. The (*E*) isomer was contaminated with a small amount of the (*Z*) isomer.

1-[(*Z*)-1-(2-Methyl-2-propoxy)-1-octen-2-yl]-1*H*-benzotriazole (8b): Oil; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 0.82 (t, *J* = 6.6 Hz, Me, 3H), 1.19-1.38 (m, $(CH_2)_4$ and *tert*-Bu, 17H), 2.64 (t, *J* = 6.9 Hz, CH_2, 2H), 6.51 (s, =CH, 1H), 7.31-7.44 (m, ArH, 3H), 8.05 (d, *J* = 8.4 Hz, ArH, 1H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 13.95, 22.47, 27.41, 27.91, 28.38, 31.37, 31.86, 77.88, 111.88, 119.51, 123.35, 124.69, 126.53, 133.58, 134.63, 145.21. Anal. Calcd for $C_{18}H_{27}N_3O$: C, 71.72; H, 9.03; N, 13.94. Found:C,72.00;H, 9.02; N, 13.61.

2-[(*Z*)-1-(2-Methyl-2-propoxy)-1-octen-2-yl]-2*H*-benzotriazole (9b): Oil; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 0.84 (t, *J* = 6.8 Hz, Me, 3H), 1.23-1.40 (m, $(CH_2)_4$ and *tert*-Bu, 17H), 2.65 (t, *J* = 6.6 Hz, CH_2, 2H), 6.50 (s, =CH, 1H), 7.34-7.37 (m, ArH, 2H), 7.89-7.92 (m, ArH, 2H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 13.98, 22.50, 27.43, 27.83, 28.37, 31.43, 31.75, 78.30, 118.19, 121.36, 125.96, 135.95, 143.96. Anal. Calcd for $C_{18}H_{27}N_3O$: C, 71.72; H, 9.03; N, 13.94. Found: C, 71.83; H, 9.04; N, 14.02.

1-[3-Propyl-1-cyclopenten-1-yl]-1*H*-benzotriazole (10): Oil; ^{1}H-NMR ($CDCl_3$) δ 0.97 (t, *J* = 7 Hz, Me, 3H), 1.43-1.60 (m, CH_2CH_2, 4H), 1.67-1.79 (m, CH, 1H), 2.27-2.38 (m, CH, 1H), 2.95-3.08 (m, CH, 1H), 3.12-3.30 (m, CH_2, 2H), 6.08 (s, =CH, 1H), 7.39 (t, *J* = 8 Hz, ArH, 1H), 7.53 (t, *J* = 8 Hz, ArH, 1H), 7.75 (d, *J* = 8 Hz, ArH, 1H), 8.08 (d, *J* = 8 Hz, ArH, 1H); ^{13}C-NMR ($CDCl_3$) δ 14.22, 20.84, 28.44, 32.28, 38.42, 44.12, 111.38, 120.07, 120.16, 124.23, 127.90, 131.81, 137.84, 146.26. This compound could not be purified due to the instability and some impurities.

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