Palladium(0)-Catalyzed Allylation of 4(5)-Substituted Imidazoles, 5(6)-Substituted Benzimidazoles, Benzotriazole and 5(6)-Methylbenzotriazole

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Pd(0)-Catalyzed allylations of 4(5)-nitroimidazole, **1**, 2-methyl-4(5)-nitroimidazole, **2**, 4(5)-bromoimidazole, **7**, 4(5)-methoxyimidazole, **10**, 5(6)-nitrobenzimidazole, **16a**, 5(6)-methylbenzimidazole, **16b**, benzotriazole, **19**, and 5(6)-methylbenzotriazole, **22**, were studied under several reaction conditions. Nitroimidazoles **1** and **2** were regioselectively allylated under thermodynamic control, leading to 1-allyl-4-nitro derivatives.

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Introduction.

The allylation of nucleophiles under Pd(0) catalysis (Tsuji-Trost reaction) is a useful synthetic method [1] and several selectivity aspects concerning the electrophilic cationic η^3 allyl complex, key intermediate in the reaction mechanism, have been reviewed [2].

However, the Tsuji-Trost reaction has another remarkable feature: it works with allylic acetates and carbonates as leaving groups, which are considered as bad leaving groups in other non palladium-mediated alkylation procedures that are kinetically controlled.

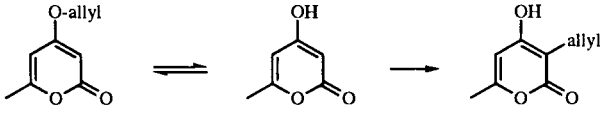


Figure 1

The Tsuji-Trost reaction can, in some cases, be conducted under thermodynamic control. The experiments summarized in Figure 1 are an example. The enolic triacetic acid lactone alkylates on oxygen to afford enol ethers under any other method [3]. However, under Pd(0) catalysis it affords the *C*-alkylated products under thermodynamic control since the conjugate base of the starting lactone (p*Ka ca* 4.9) is also a good leaving group [4]. The method has been successfully applied to heterocyclic ambident nucleophiles featuring as nucleophiles *O*- and *C*-atoms: tetronic acid [4a,5], ascorbic acid [6]; *O*- and *N*-atoms: 3-hydroxyisoxazoles [7]; *O*-, *N*- and *C*-atoms: isoxazol-5-ones [7]; *N*- and *C*-atoms: 5-pyrazolones [7], the last mentioned atom in each case being allylated under thermodynamic control.

An obvious temptation when considering which isomer is the most stable among two or more possible alkylation products from the same nucleophile is to consider the tautomeric equilibrium: the most stable tautomer would reflect the point of allylation in the most stable isomer. However, this is not necessarily so and clear notes of caution have been published [8]. The dangerous hypothesis could be true if a) steric hindrance in the alkylation products is not very important or the difference between isomers is zero and b) the tautomers of the starting material are not stabilized differently by hydrogen bonding.

It seemed to us that 1,3-diazoles could fulfill these requirements and therefore we decided to study the Tsuji-Trost reaction of several substituted imidazoles, benzimidazoles and benzotriazoles.

Results.

4(5)-Substituted Imidazoles **1, 2, 7** and **10**.

Imidazole itself has been allylated under Pd(0) catalysis [9] and of course no regioselectivity problems arise. To the best of our knowledge no substituted imidazoles have been introduced in the Tsuji-Trost reaction. It has been reported that the ratio between tautomers 1,4 and 1,5 as indicated in Figure 2 is such that $\log([1,4]/[1,5]) = 4 \times \sigma_m$ [10]. Therefore for practically any substituent, both electron-attracting or donating, the tautomer 1,4 predominates since

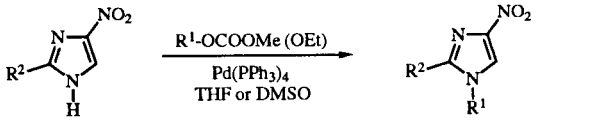
Figure 2

σ_m is dominated by inductive effects and the usual functional groups are electron-attracting by inductive mechanisms (σ_m = 0.71, 0.37 and 0.10 for $-NO_2$, -Br and $-OCH_3$).

4(5)-Nitroimidazole **1** has a p*Ka* of 9.30 and the 4-nitro tautomer predominates [11]. Alkylation of **1** with alkyl

halides and sulfates under basic conditions, through its conjugate base, affords mainly 1-alkyl-4-nitro derivatives [11]. However, treatment of **1** with dimethyl sulfate, diazomethane or alkyl *p*-toluenesulfonates in neutral medium or with alkylating agents in formic acid medium leads to 1-alkyl-5-nitroimidazoles [11,12]. Also the formation of 1-alkyl-5-nitro derivatives is described from the reaction of 2-methyl-4(5)-nitroimidazole, **2**, and alkyl polyphosphates at 160° [13]. In more recent work the influence of the temperature in the alkylation of the protonated form of **1** is reported [14]. Whereas in the experiment performed at 75° in acidic media (glacial acetic acid) 1-alkyl-5-nitro-derivatives are obtained as the major products, at 140° the thermodynamically more stable 1-alkyl-4-nitroimidazoles are formed. The thermal isomerization probably takes place through quaternization and regioselective dealkylation

Scheme 1



1 $R^2 = H$
2 $R^2 = Me$

3a $R^2 = H$; $R^1 = -CH_2-CH=CH-Ph$
3b $R^2 = H$; $R^1 = -CH_2-CH=CH_2$
3c $R^2 = H$; R^1 = 2-cyclohexenyl
4a $R^2 = Me$; $R^1 = -CH_2-CH=CH-Ph$
4b $R^2 = Me$; $R^1 = -CH_2-CH=CH_2$
4c $R^2 = Me$; R^1 = 2-cyclohexenyl

Table 1

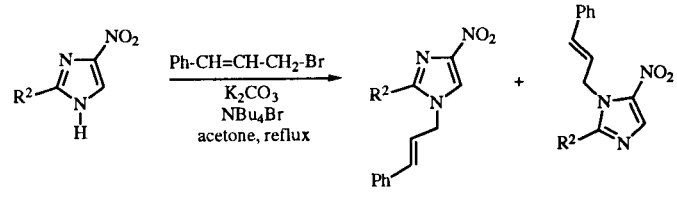
NMR and UV Data for Compounds **3** and **4**

	δ (pmr) H-5	δ (pmr) R^2	δ (cmr) R^2	δ (cmr) C-2	δ (cmr) C-4	δ (cmr) C-5	UV (log ε) (in MeOH)
3a	7.85	7.53	--	135.8	147.8	134.8	284 (3.99) 252 (4.09)
3b	7.74	7.41	--	135.8	147.9	130.6	288 (3.83)
3c	7.78	7.46	--	135.0	147.6	135.0	290 (3.84)
4a	7.75	2.46	12.7	144.6	145.8	134.8	294 (3.83) 248 (4.06)
4b	7.63	2.33	12.8	144.8	146.2	130.5	300 (3.82)
4c	7.65	2.38	13.0	143.9	145.8	134.6	302 (3.84)

Our results of palladium(0)-catalyzed allylation of 4(5)-nitroimidazole, **1**, and 2-methyl-4(5)-nitroimidazole, **2**, with three different allylic carbonates are summarized in Scheme 1. The reaction is regioselective, leading to the thermodynamic compounds **3a-c** and **4a-c** respectively. Assignments of structures **3a** and **4a** were made on the basis of the cmr spectra with the method *Selective (Long Range) Distortionless Enhancement by Polarization Transfer* (SDEPT-1D) developed by Sánchez-Ferrando and coworkers [15] in our Department. The regioisomerism is supposed to be the same in the other cases on the basis of similar spectroscopic behaviour. Some representative spectroscopic data are collected in Table 1.

The alkylation of **1** and **2** with cinnamyl bromide and potassium carbonate in the presence of *n*-tetrabutylammonium bromide afforded a mixture of 4-nitro- and 5-nitro-1-cinnamyl derivatives, **3a/5a** and **4a/6a** respectively, the former being predominant (Scheme 2). The minor isomer, **5a** or **6a**, was not isolated in pure form but characterized by a pmr signal at 5.06 (d, J = 6.2 Hz, 2H) or 5.04 (d, J = 5.5 Hz, 2H) corresponding to the cinnamylic methylene group. Some spontaneous *E/Z* isomerization was observed in the case of 4-nitro isomers **3a** and **4a**. To confirm the thermodynamic control of our allylation reaction a 71:29 mixture of **3a** and **5a** was refluxed in THF under a catalytic amount of *tetrakis*(triphenylphosphine)palladium(0), the ratio of regioisomers (pmr) being 98:2 after 24 hours (Scheme 2).

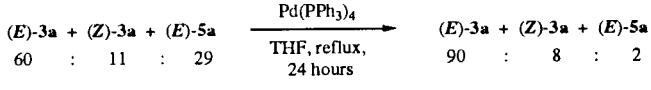
Scheme 2



1 $R^2 = H$
2 $R^2 = Me$

3a
4a

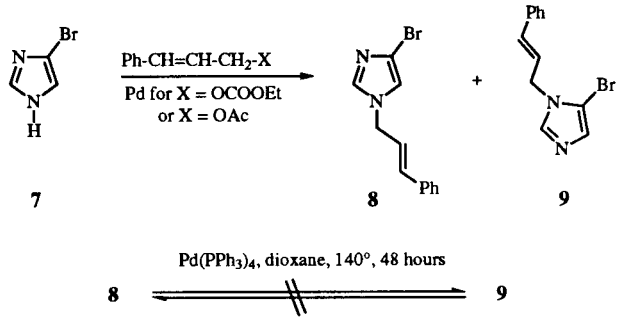
5a (86:14)
6a (91:9)



4(5)-Bromoimidazole, **7**, [16] gives mainly the 1,5-disubstituted compound when methylated with dimethyl sulfate [11a,12d]. Compound **7** affords a mixture of 4- and 5-bromo-1-methylimidazole on treatment with one or two molar equivalents of *n*-butyllithium in diethyl ether or tetrahydrofuran under various reaction conditions followed by addition of dimethyl sulfate [17]. When the alkylation of **7** is performed in two steps, deprotonation and nucleophilic displacement, the ratios of the isomeric mixtures are found to be dependent on the solvent used in the second step and on the alkylating agent [18]. Recently, Grimmett's studies on the methylation of 4(5)-substituted imidazoles (bromo and nitro derivatives among them) with dimethyl sulfate under neutral and alkaline conditions show the dependence of the ratios of regioisomers on the reaction conditions and the nature of the substituent [19].

In contrast to the nitro derivatives **1** and **2**, no good regioselectivity was attained in the Pd(0)-catalyzed allylation of 4(5)-bromoimidazole, **7**, with cinnamyl acetate or carbonate, affording mixtures of 4-bromo-1-cinnamylimi-

Scheme 3



7 8 9

dazole, **8**, and 5-bromo-1-cinnamylimidazole, **9** (Scheme 3). The ratio **8**:**9** varies depending on the experimental conditions (see Table 2). The reaction with cinnamyl ethyl carbonate and a catalytic amount of *tetrakis*(triphenylphosphine)palladium(0) in boiling THF gave the 5-bromo isomer **9** as the major compound (17:83 pmr ratio) (run 1, Table 2). Practically no isomerization takes place when the mixture is heated for 48 hours at 140° in dioxane and in the presence of *tetrakis*(triphenylphosphine)palladium(0). A similar result (30:70 ratio) was obtained when palladium acetate and triphenylphosphine anchored to a cross-linked polystyrene matrix was used as a catalytic system (run 2, Table 2). When **7** was treated with cinnamyl acetate, DBU and catalytic *bis*(1,2-diphenylphosphinoethane)palladium(0), the reverse selectivity was observed (75:25 ratio) and the isolated yields were considerably lower (run 3, Table 2). Finally, the reaction of **7** with cinnamyl bromide and potassium carbonate in boiling acetone afforded **8** and **9** in 41:59 ratio (pmr) and 51% overall yield (run 4, Table 2). The structure elucidation of the regioisomers **8** and **9** was made by a combination of bidimensional nmr techniques: GE-HMQC (*Gradient-Enhanced Heteronuclear Multiple Quantum Correlation Spectroscopy*) [20] and HMBC (*Heteronuclear Multiple Bond Connectivity*) [21].

Table 2

Allylations of 4(5)-Bromoimidazole (**7**)

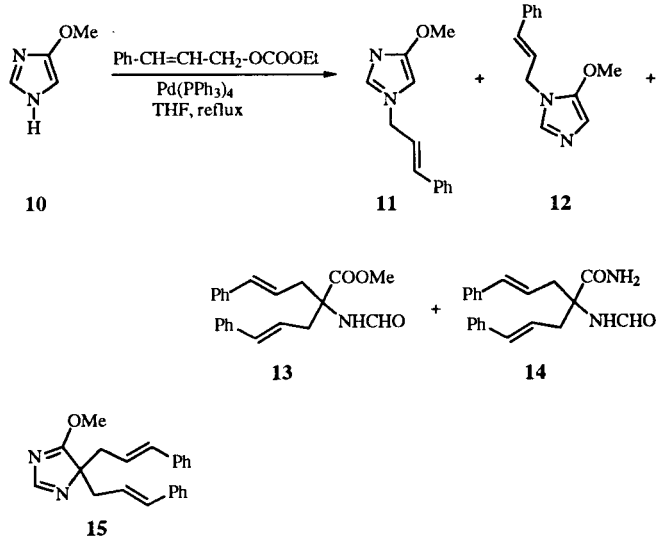
Run	Conditions	Overall %	**8**:**9** [a]
1	X = OCOOEt/$Pd(PPh_3)_4$/reflux THF/24 hours	97 [b]	17:83
2	X = OCOOEt/$Pd(OAc)_2$/[c]/reflux THF/48 hours	79 (24 + 55) [d]	30:70
3	X = OAc/DBU/$Pd(dppe)_2$/reflux THF/24 hours	36 (27 + 9) [d]	75:25
4	X = Br/K_2CO_3/NBu_4Br/reflux acetone/16 hours	51 (28 + 23) [d]	41:59

[a] Ratio determined by pmr. [b] Reaction crude. [c] Polymer-supported triphenylphosphine. [d] Isomers isolated by chromatography.

No conventional alkylations of 4(5)-methoxyimidazole, **10**, [22] have been reported. The only related work that we have found describes the reaction of 4-ethoxy-2-phenylimidazole with benzyl chloride and potassium carbonate giving rise to C-5 mono and dibenzylated compounds [23].

The allylation of 4(5)-methoxyimidazole, **10**, with cinnamyl ethyl carbonate under *tetrakis*(triphenylphosphine)palladium(0) catalysis in boiling THF (Scheme 4) gave a very complex mixture from which the following compounds could be isolated and characterized after several column chromatographies: 1-cinnamyl-4-methoxyimidazole, **11**, 1-cinnamyl-5-methoxyimidazole, **12**, methyl *N*-formyl-2,2-dicinnamylglycinate, **13**, and 2-cinnamyl-2-formylamino-5-phenyl-4-pentenamide, **14**. Compounds **13** and **14** can arise from the C-5 diallylated derivative **15** by hydrolytic opening of the ring. Also, GE-HMQC and HMBC experiments permitted structural assignment to compound **12**.

Scheme 4



10 11 12 13 14 15

5(6)-Substituted Benzimidazoles **16a,b**.

The p*K*a values in water of 5(6)-nitrobenzimidazole **16a** and 5(6)-methylbenzimidazole **16b** are 10.9 and 13.0 respectively [24]. Substituents in the positions 5(6) of the benzimidazole moiety have little influence on the tautomeric equilibrium. Thus, the K_t value for **16a** in water is 1.8 [12d]. Alkylations of 5(6)-substituted benzimidazoles with conventional alkylating agents in the presence of base give nearly equal amounts of both regioisomers [25].

As nitroimidazole derivatives **1** and **2** were found to be regioselectively allylated under Pd(0)-catalysis, we undertook similar experiments with **16a** and also with **16b** (Scheme 5, Table 3). Unfortunately only a slight predominance (62:38) of isomer 1-cinnamyl-6-nitrobenzimidazole, **17a**, over 1-cinnamyl-5-nitrobenzimidazole, **18a**, was observed in the reaction of **16a** with cinnamyl

Scheme 5

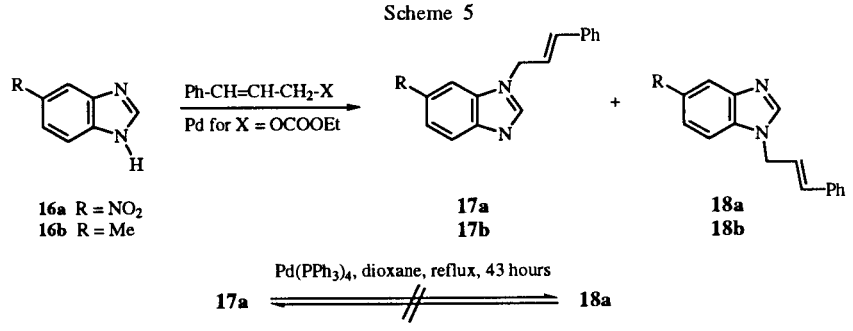


Table 3

Allylations of Benzimidazoles **16**

	Azole	Conditions	Overall %	**17:18** [a]
1	**16a**	X = OCOOEt/$Pd(PPh_3)_4$/reflux dioxane/16 hours	61	62:38
2	**16a**	X = OCOOEt/$Pd(acac)_2$/[b]/reflux dioxane/44 hours	84	56:44
3	**16a**	X = Br/K_2CO_3/reflux acetone/15 hours	76	50:50
4	**16b**	X = OCOOEt/$Pd(PPh_3)_4$/reflux dioxane/16 hours	60	50:50
5	**16b**	X = OCOOEt/$Pd(acac)_2$/[b]/reflux dioxane/72 hours	92	50:50
6	**16b**	X = Br/K_2CO_3/reflux acetone/48 hours	94	50:50

[a] Ratio determined by pmr. [b] Polymer-supported triphenylphosphine.

ethyl carbonate and *tetrakis*(triphenylphosphine)-palladium(0) in boiling dioxane (run 1, Table 3). The use of another catalytic system (palladium acetate and polymer-supported triphenylphosphine) (run 2, Table 3) did not improve the results (56:44 ratio). Under conventional conditions an equimolar mixture was obtained (run 3, Table 3). When this equimolar mixture of **17a** and **18a** was refluxed in dioxane for 43 hours in the presence of *tetrakis*(triphenylphosphine)palladium(0) no variation in the ratio of isomers was observed (Scheme 5). Compounds **17a** and **18a** were very difficult to separate by chromatography or recrystallization and pure samples were obtained only by preparative thin layer chromatography. A palladium-containing complex of stoichiometry $(C_7H_4N_3O_2)_2Pd(PPh_3)_2$ was isolated in these reactions. An spontaneous *E/Z* isomerization was also observed in **17a** and **18a**. For the 5(6)-methyl derivative **16b** no regioselectivity was found (runs 4-6, Table 3). Also in this case a metallic complex of stoichiometry $(C_8H_7N_2)_2Pd(PPh_3)_2$ precipitated from the reaction mixture. Structure assignment for the regioisomers was made by pmr (proton at C-4 of **18a** appears at lower field than proton at C-7 of **17a**, see Experimental).

Benzotriazole (**19**).

Although tautomer **19B** of benzotriazole is 4 Kcal/mol more stable than tautomer **19A** in the gas phase [26] (Figure 3), form **19A** predominates in the tautomeric equilibrium in solution [27] and in the solid phase [28]. Tautomer **19A** has a greater aromatic character [27], but the repulsion of electronic pairs in N-2 and N-3 atoms exerts a destabilizing effect [29]. The greater dipolar moment of **19A** favours the interactions between benzotriazole molecules in the solid state and between **19** and a polar solvent in solution. This fact is in accordance with **19A** being the major tautomer in the solid state and in solution.

19A **19B**

Figure 3

As benzotriazole, **19**, has a p*K*a of 8.2 [30] we considered the possibility of reversible Pd(0)-catalyzed allylation for the regioselective obtention of the most stable isomer under thermodynamic control. Two reversible reactions of **19** with Michael acceptors [31] and with aldehydes and secondary amines [32] have been described by Katritzky. On the other hand, non reversible alkylations with alkyl halides in basic medium give mixtures of N-1 and N-2 alkylated compounds [25c,33]. Regioselective alkylation at N-1 occurs in the reaction with α-haloketones in aprotic solvents and in the absence of base [34].

Scheme 6

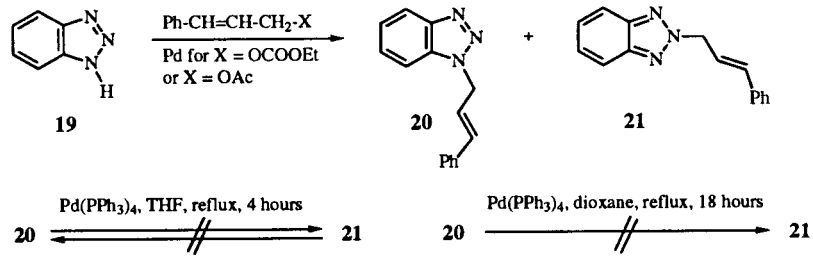


Table 4

Allylations of Benzotriazole (**19**)

Run	X	Pd/L	Base	Solvent/T(°)/t(hours)	Overall %	20:21 [a]
1	-OCOOEt	$Pd(PPh_3)_4$	--	dioxane/refl/2	74	42:58
2	-OAc	$Pd(OAc)_2/PPh_3$	DBU	THF-H_2O3:2/refl/17	[b]	60:40
3	-OAc	$Pd(PPh_3)_4$	BuLi	THF/refl/2	54	59:41
4	-OAc	$Pd(PPh_3)_4$	NaH	THF/refl/2.5	79	54:46
5	-OAc	$Pd(dppe)_2$	BuLi	THF/refl/2	[b]	44:56
6	-OAc	$Pd(OAc)_2$/[c]	BuLi	THF/refl/21	53	54:46
7	-Br	--	K_2CO_3	acetone/refl/5	96	73:27

[a] Ratio determined by pmr. [b] No product isolation was performed. [c] Polymer-supported triphenylphosphine.

Our allylation results with benzotriazole, **19**, are summarized in Scheme 6 and Table 4. Several experimental conditions were tried. In the reaction with cinnamyl ethyl carbonate under *tetrakis*(triphenylphosphine)palladium(0) catalysis in boiling dioxane a 42:58 (pmr ratio) mixture of 1-cinnamylbenzotriazole, **20**, and 2-cinnamylbenzotriazole, **21**, was obtained (run 1, Table 4). As aqueous medium can have a drastic effect on the regioselectivity of Pd(0)-catalyzed allylations [35] we decided to carry out an experiment in THF-water using cinnamyl acetate as allylating agent in the presence of DBU and the precatalytic system palladium acetate/triphenylphosphine (run 2, Table 4), but no improvements on the regioselectivity were found. Changes in the base employed (runs 3 and 4, Table 4) or the precatalytic system (runs 3, 5 and 6, Table 4) did not significantly alter the ratios obtained. Under kinetic control (cinnamyl bromide and potassium carbonate in boiling acetone) (run 7, Table 4) **20** was isolated in 70% yield. No isomerization takes place between **20** and **21** in the presence of *tetrakis*(triphenylphosphine)palladium(0) in boiling dioxane (Scheme 6).

5(6)-Methylbenzotriazole (**22**).

This compound has three different nucleophilic positions. The allylation with cinnamyl derivatives under Pd(0) catalysis and a great variety of experimental conditions (see Scheme 7 and Table 5) was not regioselective, affording in all cases mixtures of 1-cinnamyl-5-methylbenzotriazole, **23**, 1-cinnamyl-6-methylbenzotriazole, **24**, and 2-cinnamyl-5-methylbenzotriazole, **25**. In runs 1-3 cinnamyl ethyl carbonate in boiling dioxane was used with three different precatalytic systems, observing that the ratio **(23+24)/25** is reversed in runs 2-3 (where polymer-supported triphenylphosphine is present) with respect to run 1. No significant differences arose from the use of cinnamyl acetate in the presence of DBU and different catalytic systems (runs 4-6). Nevertheless, it is worth mentioning that under the conditions of run 5 (catalysis by *bis*(1,2-diphenylphosphinoethane)palladium(0), the greatest percentage of **25** is obtained. The influence of water as a cosolvent was studied in runs 7-9. Increasing percentages of water led to a greater amount of hydrolysis of cinnamyl acetate but not to a dif-

Scheme 7

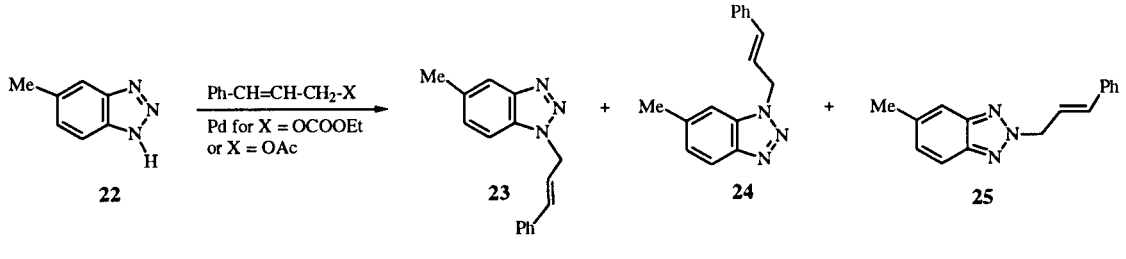


Table 5

Allylations of 5-Methylbenzotriazole (**22**)

Run	X	Pd/L	Base	Solvent/T(°)/t(hours)	**23:24:25** [a]	**(23+24):25**
1	-OCOOEt	$Pd(PPh_3)_4$	--	dioxane/refl/15.5	21:21:58	42:58
2	-OCOOEt	$Pd(acac)_2$/[b]	--	dioxane/refl/15.5	28:33:39	61:39
3	-OCOOEt	$Pd(OAc)_2$/[b]	--	dioxane/refl/15.5	27:32:41	59:41
4	-OAc	$Pd(dba)_2$/dppe	DBU	dioxane/refl/22.5	23:23:54	46:54
5	-OAc	$Pd(dppe)_2$	DBU	dioxane/refl/96	16:22:62	38:62
6	-OAc	$Pd(dba)_2$/dppb	DBU	dioxane/refl/24	19:24:57	43:57
7	-OAc	$Pd(OAc)_2/PPh_3$	DBU	THF-H_2O 4:1/refl/3	25:37:38	62:38
8	-OAc	$Pd(OAc)_2/PPh_3$	DBU	THF-H_2O 3:2/refl/3	30:32:38	62:38
9	-OAc	$Pd(OAc)_2/PPh_3$	DBU	THF-H_2O 1:4/refl/19	30:40:30	70:30
10	-OAc	$Pd(OAc)_2$/[b]	DBU	THF-H_2O 3:2/refl/64	31:40:29	71:29
11	-Br	--	K_2CO_3	acetone/refl/5	34:37:29	71:29

[a] Ratio determined by pmr. [b] Polymer-supported triphenylphosphine.

ferent ratio of regioisomers. The use of polymer-supported triphenylphosphine instead of triphenylphosphine in organic-aqueous medium (run 10, Table 5) did not improve the selectivity. From the results of the Table 5 it comes out that the use of a THF-H_2O medium or polymeric triphenylphosphine in dioxane goes in the same direction as the conventional procedure under kinetic control described in run 11 (cinnamyl bromide and potassium carbonate in boiling acetone). Structural assignment for regioisomers **23, 24** and **25** was made by pmr, the proton at C-4 in **23** appearing at lower field than the proton at C-7 of **24** due to the deshielding effect of non shared electronic pair on N-3 (see Experimental).

In summary, 4(5)-nitroimidazole, **1**, and 2-methyl-4(5)-nitroimidazole, **2**, can be regioselectively allylated under Pd(0) catalysis, affording the 1-allyl-4-nitro derivatives under thermodynamic control. Allylations of the other azoles studied take place under kinetic control, no reversibility being observed.

EXPERIMENTAL

The pmr (cmr) spectra were registered at 250 or 400 MHz (62.5 or 100 MHz) using tetramethylsilane as the internal standard. Mass spectra were determined under electron impact (70 eV). In polymer-supported triphenylphosphine the polymer is polystyrene cross-linked with 2% divinylbenzene (3 mmoles P/g polymer) (Aldrich, ref. 36, 645-5).

1-Cinnamyl-4-nitroimidazole (**3a**).

A solution of **1** (4.080 g, 36 mmoles), *tetrakis*(triphenylphosphine)palladium(0) (2.020 g, 1.75 mmoles) and cinnamyl methyl carbonate (6.920 g, 36 mmoles) in anhydrous and degassed dimethyl sulfoxide (175 ml) was heated under argon and magnetic stirring at 80-85° for 4 hours (tlc monitoring). The crude mixture was partitioned between dichloromethane and water. The organic phase was washed several times with water, dried with anhydrous sodium sulfate and the solvent evaporated. The residue was chromatographed through silica gel (230-400 mesh) under pressure with dichloromethane-ethyl acetate mixtures of increasing polarity as the eluent, affording **3a** as a yellowish solid. It was recrystallized from diethyl ether (white solid, 5.520 g, 67% yield), mp 82-83°; ir (potassium bromide): 1544, 1525, 1487, 1372, 1335, 1281 cm^{-1}; uv (methanol): λ max 284 (log ε 3.99), 252 (log e 4.09) nm; pmr (deuteriochloroform): 4.78 (d, J = 6.7 Hz, 2H), 6.27 (dt, J = 15.9 Hz, J = 6.7 Hz, 1H), 6.65 (d, J = 15.9 Hz, 1H), 7.27-7.39 (m, 5H), 7.53 (s, 1H), 7.85 (s, 1H); cmr (deuteriochloroform): 50.0, 119.3, 121.0, 126.5, 128.5, 134.8, 135.7, 135.8, 147.8.

Anal. Calcd. for $C_{12}H_{11}N_3O_2$: C, 62.87; H, 4.84; N, 18.33. Found: C, 62.82; H, 4.87; N, 18.34.

Compounds **3b-c** were prepared as for **3a**. An analogous procedure was followed for **4a-c**, except that tetrahydrofuran at reflux temperature was used.

1-Allyl-4-nitroimidazole (**3b**).

This compound was obtained in 83% yield after chromatography, mp 48-50° (chloroform); ir (potassium bromide): 1547, 1527, 1484, 1379, 1344, 1288 cm^{-1}; uv (methanol): λ max 288 (log ε 3.83) nm; pmr (deuteriochloroform): 4.60 (broad d, J = 6.2 Hz, 2H), 5.24 (broad d, J = 16.8 Hz, 1H), 5.33 (broad d, J = 10.2 Hz, 1H), 5.92 (ddt, J = 16.8 Hz, J = 10.2 Hz, J = 6.2 Hz, 1H), 7.41 (d, J = 1.0 Hz, 1H), 7.74 (d, J = 1.0 Hz, 1H); cmr (deuteriochloroform): 50.4, 119.3, 120.7, 130.6, 135.8, 147.9.

Anal. Calcd. for $C_6H_7N_3O_2$: C, 47.06; H, 4.61; N, 27.44. Found: C, 47.52; H, 4.51; N, 26.71.

1-(2-Cyclohexen-1-yl)-4-nitroimidazole (**3c**).

This compound was obtained in 84% yield after chromatography, mp 29-31° (dichloromethane-diethyl ether); ir (film): 1539, 1511, 1490, 1398, 1335, 1286 cm^{-1}; uv (methanol): λ max 290 (log ε 3.84) nm; pmr (deuteriochloroform): 1.50-1.90 (m, 3H), 1.95-2.25 (m, 3H), 4.76 (m, 1H), 5.68 (ddt, J = 10.0 Hz, J = 3.7 Hz, J = 2.0 Hz, 1H), 6.15 (ddt, J = 10.0 Hz, J = 4.0 Hz, J = 1.8 Hz, 1H), 7.46 (d, J = 1.5 Hz, 1H), 7.78 (d, J = 1.5 Hz, 1H); cmr (deuteriochloroform): 18.5, 24.3, 31.3, 53.8, 118.4, 130.0, 135.0, 147.7.

Anal. Calcd. for $C_9H_{11}N_3O_2$: C, 55.95; H, 5.74; N, 21.75. Found: C, 56.14; H, 5.44; N, 21.28.

1-Cinnamyl-2-methyl-4-nitroimidazole (**4a**).

This compound was obtained in 88% yield after chromatography, mp 96-98.5° (diethyl ether); uv (methanol): λ max 294 (log ε 3.83), 248 (log ε 4.06) nm; ir (potassium bromide): 1535, 1496, 1398, 1330, 1292 cm^{-1}; pmr (deuteriochloroform): 2.43 (s, 3H), 4.67 (dd, J = 6.1 Hz, J = 1.2 Hz, 2H), 6.21 (dt, J = 15.9 Hz, J = 6.1 Hz, 1H), 6.49 (d, J = 15.9 Hz, 1H), 7.26-7.36 (m, 5H), 7.73 (s, 1H); cmr (deuteriochloroform): 12.7, 48.7, 119.7, 121.0, 126.3, 128.2, 128.3, 134.4, 134.8, 144.6, 145.8.

Anal. Calcd. for $C_{13}H_{13}N_3O_2$: C, 64.19; H, 5.39; N, 17.27. Found: C, 64.21; H, 5.39; N, 17.26.

1-Allyl-2-methyl-4-nitroimidazole (**4b**).

This compound was obtained in 85% yield after chromatography, mp 65-67° (chloroform) (lit [14] 62-64°); uv (methanol): λ max 300 (log ε 3.82); ir (potassium bromide): 1546, 1504, 1391, 1328, 1286 cm^{-1}; pmr (deuteriochloroform): 2.33 (s, 3H), 4.49 (apparent dt, J = 5.5 Hz, J *ca* 1.5 Hz, 2H), 5.06 (apparent dt, J = 17.0 Hz, J *ca* 1.5 Hz, 1H), 5.30 (apparent dt, J = 10.2 Hz, J *ca* 1.5 Hz, 1H), 5.87 (ddt, J = 17.0 Hz, J = 10.2 Hz, J = 5.5 Hz, 1H), 7.63 (s, 1H); cmr (deuteriochloroform): 12.8, 49.2, 119.4, 119.7, 130.5, 144.8, 146.1.

Anal. Calcd. for $C_7H_9N_3O_2$: C, 50.30; H, 5.43; N, 25.14. Found: C, 50.47; H, 5.13; N, 24.74.

1-(2-Cyclohexen-1-yl)-2-methyl-4-nitroimidazole (**4c**).

This compound was obtained in 90% yield after chromatography, mp 84-86° (dichloromethane-diethyl ether); uv (methanol): λ max 302 (log ε 3.84) nm; ir (potassium bromide): 1539, 1490, 1455, 1405, 1342, 1265 cm^{-1}; pmr (deuteriochloroform): 1.56-1.73 (m, 3H), 1.95-2.15 (m, 3H); 2.38 (s, 3H), 4.60-4.70 (m, 1H), 5.60 (ddt, J = 10.1 Hz, J = 5.5 Hz, J = 2.0 Hz, 1H), 6.12 (ddt, J = 10.1 Hz, J = 4.0 Hz, J = 2.0 Hz, 1H), 7.65 (s, 1H); cmr (deuteriochloroform): 13.0, 18.4, 24.2, 30.0, 52.2, 118.3, 123.5, 134.6, 144.0, 145.8.

Anal. Calcd. for $C_{10}H_{13}N_3O_2$: C, 57.96; H, 6.32; N, 20.38. Found: C, 57.95; H, 6.08; N, 19.96.

Allylation of **1** with Cinnamyl Bromide and Potassium Carbonate.

A mixture of **1** (1.131 g, 10.0 mmoles), cinnamyl bromide (1.971 g, 10.0 mmoles), potassium carbonate (2.073 g, 15.0 mmoles), tetrabutylammonium bromide (0.033 g, 0.1 mmole) and acetone (100 ml) was refluxed for 3 hours (tlc monitoring). The solid was filtered off and the solvent from the filtrate was evaporated to afford a 86:14 mixture of **3a** and 1-cinamyl-5-nitroimidazole, **5a** (1.921 g, 83% overall yield). Only a small amount of the minor isomer **5a** could be separated in pure form as an oil after column chromatography through silica gel (230-400 mesh) under pressure; pmr (deuteriochloroform) of **5a**: 5.06 (d, J = 6.2 Hz, 2H), 6.24 (dt, J = 15.7 Hz, J = 6.2 Hz, 1H), 6.56 (d, J = 15.7 Hz, 1H), 7.20-7.33 (m, 5H), 7.61 (s, 1H), 7.96 (s, 1H).

Allylation of **2** with Cinnamyl Bromide and Potassium Carbonate.

Following the same procedure described above a 91:9 mixture of **4a** and 1-cinnamyl-2-methyl-5-nitroimidazole, **6a**, was obtained. The minor isomer **6a** could not be separated in pure form and its pmr spectrum was deduced from that of the mixture; pmr (deuteriochloroform) of **6a**: 2.49 (s, 3H), 5.04 (d, J = 5.5 Hz, 2H), 6.20 (m, 1H), 6.40 (broad d, J = 15.2 Hz, 1H), 7.30 (m, 5H), 7.94 (s, 1H).

Allylation of 4(5)-Bromoimidazole, **7**, with Cinnamyl Ethyl Carbonate under Palladium(II) Acetate/Polymer-supported Triphenylphosphine Catalysis (run 2, Table 2).

A degassed mixture of **7** [16] (0.074 g, 0.50 mmole), cinnamyl ethyl carbonate (0.125 g, 0.60 mmole), palladium(II) acetate (0.012 g, 0.05 mmole), polymer-supported triphenylphosphine (0.167 g, 0.50 mmole) and anhydrous tetrahydrofuran (20 ml) was refluxed under nitrogen for 48 hours (pmr monitoring). The polymer was filtered off, the solvent from the filtrate was evaporated and the residue was chromatographed through silica gel (230-400 mesh) under pressure. Eluting with mixtures of hexanes-ethyl acetate of increasing polarity the following compounds were separated:

4-Bromo-1-cinnamylimidazole, **8**, (0.032 g, 24% yield), showed mp 81-83° (diethyl ether); ir (potassium bromide): 1478, 1389, 1237, 968, 942 cm^{-1}; pmr (deuteriochloroform): 4.65 (dd, J = 5.9 Hz, J = 1.5 Hz, 2H), 6.22 (dt, J = 15.5 Hz, J = 5.9 Hz, 1H), 6.55 (d, J = 15.5 Hz, 1H), 6.92 (d, J = 1.5 Hz, 1H), 7.24-7.40 (m, 6H); cmr (deuteriochloroform): 49.4, 115.3, 118.1, 122.5, 126.5, 128.4, 128.6, 134.4, 135.3, 136.5.

Anal. Calcd. for $C_{12}H_{11}BrN_2$: C, 54.77; H, 4.21; N, 10.65. Found: C, 54.87; H, 4.04; N, 10.62.

5-Bromo-1-cinnamylimidazole, **9** (0.072 g, 55% yield), showed bp 130-140° (oven temperature)/0.5 mm Hg; ir (film): 1471, 1227, 1107, 966, 904, 755, 691, 658 cm^{-1}; pmr (deuteriochloroform): 4.66 (dd, J = 5.9 Hz, J = 1.1 Hz, 2H), 6.20 (dt, J = 15.7 Hz, J = 5.9 Hz, 1H), 6.43 (d, J = 15.7 Hz, 1H), 7.03 (br s, 1H), 7.21-7.34 (m, 5H), 7.58 (br s, 1H); cmr (deuteriochloroform): 47.8, 103.1, 122.6, 126.5, 128.3, 128.6, 129.7, 133.9, 135.6, 137.7.

Anal. Calcd. for $C_{12}H_{11}BrN_2$: C, 54.77; H, 4.21; N, 10.65. Found: C, 54.66; H, 4.57; N, 10.39.

Allylation of **7** with Cinnamyl Acetate under *bis*(1,2-Diphenylphosphinoethane)palladium(0) Catalysis (run 3, Table 2).

To a magnetically stirred and degassed solution of **7** (0.500 g, 3.4 mmoles) and DBU (0.520 g, 3.4 mmoles) in anhydrous tetrahydrofuran (20 ml) was added a degassed solution of cinnamyl acetate (0.720 g, 4.1 mmoles) and *bis*(1,2-diphenylphosphinoethane)palladium(0) (0.154 g, 0.17 mmole) in anhydrous tetrahydrofuran (15 ml). The reaction mixture was refluxed under nitrogen for 24 hours (tlc monitoring), then ethyl acetate (50 ml) was added and the organic solution washed with 1*M* hydrochloric acid (3 x 50 ml) and water (2 x 50 ml). The organic phase was dried with anhydrous sodium sulfate, the solvent was evaporated and the residue chromatographed through silica gel (230-400 mesh) under pressure to afford **8** (0.240 g, 27% yield) and **9** (0.085 g, 9% yield).

Allylation of 4(5)-Methoxyimidazole **10** [19] with Cinnamyl Ethyl Carbonate under *tetrakis*(Triphenylphosphine)palladium(0) Catalysis.

A degassed solution of **10** (0.500 g, 5.1 mmoles), cinnamyl ethyl carbonate (1.160 g, 5.6 mmoles) and *tetrakis*(triphenylphosphine)palladium(0) (0.300 g, 0.25 mmole) in anhydrous tetrahydrofuran (35 ml) was refluxed under nitrogen for 21 hours (tlc monitoring). The solvent was evaporated and the residue was chromatographed through a silica gel column under pressure. Elution with chloroform-acetone mixtures of increasing polarity allowed the separation and identification of the following fractions:

A reddish oil (0.185 g) which was purified by another column chromatography on silica gel under pressure with hexanes ethyl acetate 4:1 as eluent; methyl *N*-formyl-2,2-dicinnamylglycinate, **13**, (0.086 g, 5% yield) was thus obtained as a yellowish oil which became a white solid after microdistillation, bp 200-210° (oven temperature)/0.5 mm Hg, mp 108-110°; ir (potassium bromide): 3245 (br), 1743, 1657 cm^{-1}; pmr (deuteriochloroform): 2.74 (dd, J = 13.9 Hz, J = 7.7 Hz, 2H), 3.39 (dd, J = 13.9, J = 7.7 Hz, 2H), 3.79 (s, 3H), 5.94 (dt, J = 15.7 Hz, J = 7.7 Hz, 2H), 6.43 (d, J = 15.7 Hz, 2H), 7.18-7.27 (m, 10H), 8.18 (d, J = 1.8 Hz, 1H); cmr (deuteriochloroform): 38.6, 52.9, 65.0, 123.0, 126.1, 127.4, 128.4, 134.3, 136.8, 160.1, 172.9; ms: (m/z) 350 (M+1, 6), 349 (M, 6), 304 (22), 117 (98), 115 (100), 91 (88).

Anal. Calcd. for $C_{22}H_{23}NO_3$: C, 75.62; H, 6.63; N, 4.01. Found: C, 75.47; H, 6.36; N, 3.96.

A brown oil (0.230 g) which was an inseparable mixture (54:46 pmr ratio) of triphenylphosphine oxide and 1-cinnamyl-4-methoxyimidazole, **11** (0.124 g, 11% yield based on pmr integration); pmr (deuteriochloroform): 3.76 (s, 3H), 4.56 (d, J = 6.2 Hz, 2H), 6.21 (dt, J = 15.7 Hz, J = 6.2 Hz, 1H), 6.22 (d, J = 1.5 Hz, 1H), 6.52 (d, J = 15.7 Hz, 1H), 7.14 (d, J = 1.5 Hz, 1H), 7.22-7.32 (m, 5H).

A brown oil which was characterized as 1-cinnamyl-5-methoxyimidazole, **12** (0.185 g, 17% yield); ir (film): 1581, 1504, 1032, 969, 737, 695 cm^{-1}; pmr (deuteriochloroform): 3.71 (s, 3H), 4.38 (d, J = 5.9 Hz, 2H), 6.10 (dt, J = 15.7 Hz, J = 5.9 Hz, 1H), 6.20 (s, 1H), 6.32 (d, J = 15.7 Hz, 1H), 7.03 (s, 1H), 7.11-7.21 (m, 5H); cmr (deuteriochloroform): 44.7, 58.1, 103.8, 123.5, 126.3, 127.8, 128.4, 130.1, 132.7, 135.8, 148.0; ms: (m/z) 214 (M, 13), 117 (100).

A reddish oil (0.147 g) which upon digestion in diethyl ether afforded 2-cinnamyl-2-formylamino-5-phenyl-4-pentenamide, **14**, as a white solid (0.037 g, 2% yield), mp 176-178°; ir (potassium bromide): 3438, 3398, 3201, 1673 cm^{-1}; pmr (deuteriochloroform): 2.83 (ddd, J = 14.3 Hz, J = 6.6 Hz, J = 1.1 Hz, 2H), 3.18 (dd, J = 14.3 Hz, J = 8.4 Hz, 2H), 5.55 (br s, 1H), 6.07 (ddd, J = 15.7 Hz, J = 8.4 Hz, J = 6.6 Hz, 2H), 6.33 (br s, 2H), 6.49 (d, J = 15.7 Hz, 2H), 7.18-7.33 (m, 10H), 8.17 (d, J = 1.8 Hz, 1H); cmr (deuteriochloroform): 39.2, 63.9, 122.8, 126.3, 127.7, 128.6, 134.9, 136.7, 160.9, 174.0; me: (m/z) 334 (M, 0.2), 316 (9), 289 (18), 117 (100), 115 (40), 91 (24).

A complex mixture (dark oil, 0.203 g) from which pure products could not be isolated.

Compound **10** (0.058 g, 12%) was partially recovered.

Allylation of 5(6)-Nitrobenzimidazole, **16a**, with Cinnamyl Ethyl Carbonate under *tetrakis*(Triphenylphosphine)palladium-(0) Catalysis (run 1, Table 3).

A degassed solution of **16a** (0.979 g, 6.0 mmoles), cinnamyl ethyl carbonate (1.237 g, 6.0 mmoles) and *tetrakis*(triphenylphosphine)palladium(0) (0.347 g, 0.3 mmole) in anhydrous dioxane (20 ml) was refluxed under nitrogen for 16 hours (tlc monitoring). The brown solid which formed was filtered (0.103 g, 36% yield for $(C_7H_4N_3O)_2)_2Pd(PPh_3)_2$), mp >300°; ir (potassium bromide): 1609, 1518, 1468, 1342, 1314, 1293, 1187, 1068, 871, 793, 695 cm^{-1}. The solvent from the filtrate was evaporated. The residue was a mixture of 1-cinnamyl-6-nitrobenzimidazole, **17a**, 1-cinnamyl-5-nitrobenzimidazole, **18a**, and triphenylphosphine oxide. Attempted separation of **17a** and **18a** by column chromatography and recrystallization was unsuccessful (61% overall isolated yield, 62:38 ratio). Pure samples of both compounds were obtained by preparative thin layer chromatography eluting first with hexanes-ethyl acetate 3:2 and then with ethyl acetate. Partial *E/Z* isomerization was observed in both compounds (60:40 *E/Z* equilibrium ratio). Compound **17a** had pmr (deuteriochloroform): (*E* form) 5.05 (dd, J = 6.2 Hz, J = 1.5 Hz, 2H), 6.32 (dt, J = 15.7 Hz, J = 6.2 Hz, 1H), 6.63 (dt, J = 15.7 Hz, J = 1.5 Hz, 1H), 7.20-7.40 (m, 5H), 7.85 (d, J = 9.1 Hz, 1H), 8.18 (s, 1H), 8.20 (dd, J = 9.1 Hz, J = 2.2 Hz, 1H), 8.39 (d, J = 2.2 Hz, 1H); pmr (deuteriochloroform) (*Z* form): 5.09 (dd, J = 6.6 Hz, J = 1.8 Hz, 2H), 5.81 (dt, J = 11.3 Hz, J = 6.6 Hz, 1H), 6.89 (d, J = 11.3 Hz, 1H), 7.20-7-40 (m, 6H), 7.81 (d, J = 9.1 Hz, 1H), 8.11 (s, 1H), 8.14 (d, J = 2.2 Hz, 1H); cmr (deuteriochloroform) (*E/Z* mixture): 43.4, 47.4, 106.9, 107.0, 117.9, 118.0, 120.4, 120.5, 121.4, 123.9, 126.6 (double), 128.2, 128.5, 128.6, 128.7 (double), 128.7, 134.9, 135.1, 143.7, 143.8, 146.8 (double), 147.2 (double), 148.1 (double).

Compound **18a** had pmr (deuteriochloroform): (*E* form) 5.02 (dd, J = 6.2 Hz, J = 1.5 Hz, 2H), 6.34 (dt, J = 15.7 Hz, J = 6.2 Hz, 1H), 6.63 (dt, J = 15.7 Hz, J = 1.5 Hz, 1H), 7.20-7.40 (m, 5H), 7.52 (d, J = 9.0 Hz, 1H), 8.17 (s, 1H), 8.25 (dd, J = 9.0 Hz, J = 2.2 Hz, 1H), 8.76 (d, J = 2.2 Hz, 1H), pmr (deuteriocloroform): (*Z* form) 5.11 (dd, J = 6.6 Hz, J = 1.8 Hz, 2H), 5.67 (dt, J = 11.3 Hz, J = 6.6 Hz, 1H), 6.89 (d, J = 11.3 Hz, 1H), 7.20-7.40 (m, 6H), 8.10 (s, 1H), 8.19 (dd, J = 9.1 Hz, J = 2.2 Hz, 1H), 8.72 (d, J = 2.2 Hz, 1H); cmr (deuteriochloroform): (*E* form) 47.1, 109.8, 116.6, 118.3, 121.4, 121.5, 126.3, 128.4, 132.8, 134.2, 134.9, 137.6, 142.8, 143.2.

Anal. (mixture of **17a** and **18a**) Calcd. for $C_{16}H_{13}N_3O_2$: C, 68.81; H, 4.69; N, 15.04. Found: C, 68.98; H, 4.55; N, 14.84.

Allylation of 5(6)-Methylbenzimidazole, **16b** with Cinnamyl Ethyl Carbonate under *tetrakis*(Triphenylphosphine)-palladium(0) Catalysis (run 4, Table 3).

A degassed solution of **16b** (1.057 g, 8.0 mmoles), cinnamyl ethyl carbonate (1.650 g, 8.0 mmoles) and *tetrakis*(triphenylphosphine)palladium(0) (0.462 g, 0.4 mmole) in anhydrous dioxane (20 ml) was refluxed under nitrogen for 16 hours. The brown solid formed was filtered (0.127 g, 35% yield for $(C_8H_7N_2)_2Pd(PPh_3)_2$), mp >300°; ir (potassium bromide): 1616, 1482, 1285, 1236, 1096, 800, 695 cm^{-1}. The solvent from the filtrate was evaporated and the residue was chromatographed through a silica gel column with hexanes-ethyl acetate mixtures of increasing polarity as eluents. The following fractions were separated:

A mixture of 1-cinnamyl-6-methylbenzimidazole, **17b**, and 1-cinnamyl-5-methylbenzimidazole, **18b** (oil, 1.040 g, 50:50 pmr ratio), from which upon digestion on diethyl ether, a pure sample of **18b** was obtained as a white solid (0.122 g), mp 117-118° (diethyl ether); pmr (deuteriochloroform): 2.45 (s, 3H), 4.89 (d, J = 5.8 Hz, 2H), 6.29 (dt, J = 16.1 Hz, J = 5.8 Hz, 1H), 6.53 (d, J = 16.1 Hz, 1H), 7.08 (d, J = 8.0 Hz, 1H), 7.20-7.32 (m, 6H), 7.58 (s, 1H), 7.88 (s, 1H); cmr (deuteriochloroform): 21.3, 46.8, 109.3, 119.9, 122.9, 124.3, 126.4, 128.1, 128.5, 131.7, 131.8, 133.3, 135.5, 142.6, 144.2.

Anal. Calcd. for $C_{17}H_{16}N_2$: C, 82.22; H, 6.49; N, 11.28. Found: C, 82.20; H, 6.50; N, 11.37.

Compound **17b** that was not obtained in pure form and its spectroscopic data were deduced from the mixture of regioisomers; pmr (deuteriochloroform): 2.43 (s, 3H), 4.77 (d, J = 5.8 Hz, 2H), 6.21 (dt, J = 16.1 Hz, J = 5.8 Hz, 1H), 6.46 (d, J = 16.1 Hz, 1H), 7.14 (s, 1H), 7.18-7.26 (m, 6H), 7.68 (d, J = 8.4 Hz, 1H), 7.79 (s, 1H); cmr (deuteriochloroform): 21.6, 46.5, 109.5, 119.6, 122.9, 123.6, 126.3 (double), 128.0, 128.4 (double), 131.9, 132.7, 133.1, 133.9, 141.8, 142.2.

Compound **16b** (0.253 g, 24 %) was partially recovered.

Allylation of Benzotriazole, **19**, with Cinnamyl Ethyl Carbonate under *tetrakis*(Triphenylphosphine)palladium(0) Catalysis (run 1, Table 4).

A degassed and magnetically stirred solution of **19** (0.953 g, 8.0 mmoles), cinnamyl ethyl carbonate (1.649 g, 8.0 mmoles) and *tetrakis*(triphenylphosphine)palladium(0) (0.462 g, 0.4 mmole) in anhydrous dioxane (20 ml) was kept under argon at room temperature for 3 hours and then refluxed for 2 hours. The solvent was evaporated and the residue chromatographed through a silica gel column with hexanes-ethyl acetate mixtures of increasing polarity as eluents, the following compounds being obtained:

2-Cinnamylbenzotriazole, **21**, (0.785 g, 42% yield), had mp 57-58° (hexane-ethyl acetate 19:1); ir (potassium bromide): 1567, 1496, 1447, 1433, 1321, 1264, 1166, 969, 871, 744, 709, 688 cm^{-1}; pmr (deuteriochloroform): 5.46 (dd, J = 6.6 Hz, J = 1.1 Hz, 2H), 6.51 (dt, J = 15.7 Hz, J = 6.6 Hz, 1H), 6.75 (d, J = 15.7 Hz, 1H), 7.20-7.40 (m, 5H), 7.36 (AA'XX' system, 2H), 7.85 (AA'XX' system, 2H); cmr (deuteriochloroform): 58.5, 118.0, 122.0, 126.4, 126.8, 128.3, 128.6, 135.2, 135.7, 144.5.

Anal. Calcd. for $C_{15}H_{13}N_3$: C, 76.57; H, 5.57; N, 17.86. Found: C, 76.61; H, 5.60; N, 17.80.

1-Cinnamylbenzotriazole, **20**, (0.531 g, 32% yield), had mp 75-76° (hexane); ir (film): 1497, 1447, 1265, 1227, 1105, 969, 779, 751, 688 cm^{-1}; pmr (deuteriochloroform): 5.36 (dd, J = 6.2 Hz, J = 1.5 Hz, 2H), 6.36 (dt, J = 15.7 Hz, J = 6.2 Hz, 1H), 6.65 (dt, J = 15.7 Hz, J = 1.5 Hz, 1H), 7.20-7.45 (m, 7H), 7.54 (dt, J = 8.4 Hz, J = 1.1 Hz, 1H), 8.05 (dt, J = 8.4 Hz, J = 1.1 Hz, 1H); cmr (deuteriochloroform): 50.2, 109.5, 119.6, 121.9, 123.7, 126.3, 127.1, 128.0, 128.3, 132.6, 134.0, 135.3, 145.9.

Anal. Calcd. for $C_{15}H_{13}N_3$: C, 76.57; H, 5.57; N, 17.86. Found: C, 76.71; H, 5.56; N, 17.75.

Allylation of 5(6)-Methylbenzotriazole, **22**, with Cinnamyl Ethyl Acetate under *tetrakis*-(Triphenylphosphine)palladium(0) Catalysis (run 1, Table 5).

A degassed solution of **22** (0.799 g, 6.0 mmoles), cinnamyl ethyl carbonate (1.237 g, 6.0 mmoles) and *tetrakis*(triphenylphosphine)palladium(0) (0.347 g, 0.3 mmole) in anhydrous dioxane (20 ml) was refluxed under nitrogen for 15.5 hours (tlc monitoring). Upon evaporation of the solvent and silica gel column chromatography of the residue (1.838 g) with hexanes-ethyl acetate mixtures of increasing polarity as eluents, the following fractions were obtained:

2-Cinnamyl-5-methylbenzotriazole, **25**, (0.776 g, 52% yield) was obtained as an oil which crystallized spontaneously, mp 52-53° (diethyl ether); ir (potassium bromide): 1558, 1496, 1449, 1377, 1332, 1254, 1231, 1187, 999, 968, 872, 811, 771, 748, 711, 691 cm^{-1}; pmr (deuteriochloroform): 2.40 (s, 3H), 5.37 (d, J = 6.6 Hz, 2H), 6.46 (dt, J = 15.7 Hz, J = 6.6 Hz, 1H), 6.66 (d, J = 15.7 Hz, 1H), 7.13 (d, J = 8.8 Hz, 1H), 7.19-7.32 (m, 5H), 7.57 (s, 1H), 7.72 (d, J = 8.8 Hz, 1H); cmr (deuteriochloroform): 21.8, 58.1, 116.0, 117.2, 121.9, 126.5, 128.0, 128.3, 134.7, 135.5, 136.1, 142.9, 144.8.

Anal. Calcd. for $C_{16}H_{15}N_3$: C, 77.08; H, 6.06; N, 16.85. Found: C, 77.02; H, 6.09; N, 16.79.

A mixture of 1-cinnamyl-5-methylbenzotriazole, **23**, and 1-cinnamyl-6-methylbenzotriazole, **24**, was obtained as an oil which crystallized spontaneously (0.568 g, 38% overall yield, 1:1 pmr ratio). A sample of **24** with a purity of 92% was obtained after two recrystallizations in diethyl ether, mp 93-95°; ir (potassium bromide): 1622, 1496, 1454, 1258, 1218, 1106, 1060, 1040, 971, 809, 780, 757, 690 cm^{-1}; pmr (deuteriochloroform): 2.48 (s, 3H), 5.36 (dd, J = 6.2 Hz, J = 1.1 Hz, 2H), 6.36 (dt, J = 15.7 Hz, J = 6.2 Hz, 1H), 6.62 (d, J = 15.7 Hz, 1H), 7.17 (d, J = 8.8 Hz, 1H), 7.23-7.35 (m, 6H), 7.93 (d, J = 8.8 Hz, 1H); cmr (deuteriochloroform): 21.7, 49.9, 108.6, 119.1, 122.1, 126.0, 126.3, 128.0, 128.4, 133.1, 133.8, 135.4, 137.7, 144.6. Spectroscopic data of **23** were deduced from the spectra of the mixture; pmr (deuteriochloroform): 2.48 (s, 3H), 5.38 (dd, J = 6.2 Hz, J = 1.1 Hz, 2H), 6.35 (dt, J = 15.7 Hz, J = 6.2 Hz, 1H), 6.63 (d, J = 15.7 Hz, 1H), 7.23-7.35 (m, 6H), 7.41 (d, J = 8.4 Hz, 1H), 7.80 (s, 1H); cmr (deuteriochloroform): 21.1, 50.2, 109.0, 118.5, 122.0, 126.3, 128.3, 129.2, 131.1, 133.6, 133.9, 135.3, 137.7, 146.6.

Anal. (mixture of **23** and **24**) Calcd. for $C_{16}H_{15}N_3$: C, 77.08; H, 6.06; N, 16.85. Found: C, 76.79; H, 5.69; N, 16.92.

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