J. Org. Chem. **1992**, *57*, 157-162

C4), 66.0 (d, C5′, J = 5.2 Hz), 61.8 (C6), 51.77 (d, C2, J = 9.1 Hz).

Chemical Acetylation of 6. The crude reaction mixture obtained from the preceding step was concentrated to 100 mL at reduced pressure, and N-acetoxysuccinimide[65] (~90%, 2.63 g, ~15 mmol), dissolved in a mixture of water/THF (30 mL, 1/1, v/v), was added to the stirred solution at rt. The pH of the reaction was controlled at ~7.5 by the addition of 5 N NaOH. After 7 h the pH was constant and the product purification was accomplished as described above for **5**. Compound **7** was obtained as the disodium salt (1.75 g, 34% yield), a white powder, which was indistinguishable by ^1H and ^{13}C NMR spectroscopy from authentic material: ^1H NMR (D_2O, 400 MHz) δ 7.94 (d, H6″, J = 8.1 Hz), 5.97 (d, H1′, J = 4.7 Hz), 5.95 (d, H5″, J = 8.1 Hz), 5.54 (dd, H1, J = 7.1, 3.3 Hz), 4.45–4.30 (m, H2′, H3′), 4.30–4.16 (m, H4′, H5′a, H5′b, H2, H5), 4.04 (br d, H4, J = 2.5 Hz), 3.96 (dd, H3, J = 11.0, 3.1 Hz), 3.78 (dd, H6a, J = 7.2, 11.8 Hz), 3.73 (dd, H6b, J = 5.2, 11.8 Hz), 2.08 (s, CH_3); ^{13}C NMR (D_2O, 100 MHz) δ 175.8 (C=O, Ac), 167.1 (C4″), 152.7 (C2″), 142.5 C6″), 103.5 (C5″), 95.5 (d, C1, J = 6.1 Hz), 89.4 (C1′), 84.1 (d, C4′, J = 9.1 Hz), 74.6 (C3′), 72.9 (C5), 70.5 (C2′), 69.2 (C4), 68.5 (C3), 65.9 (d, C5′, J = 5.6 Hz), 61.9 (C6), 50.62 (d, C2, J = 8.0 Hz), 23.0 (CH_3, Ac).

Regiospecific Palladium-Catalyzed Cycloaddition of Aziridines and Carbodiimides

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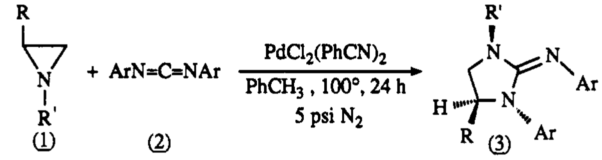
Bis(benzonitrile)palladium dichloride is an effective catalyst for the cycloaddition reaction of aziridines with carbodiimides to form imidazolidenimines in 40–94% yields. The process is a regiospecific one, involving cleavage of the more substituted ring carbon–nitrogen bond. An X-ray structure determination of one of the imidazolidinimines, together with spectral and analytical data for the products of all the cycloaddition reactions, provided the basis for the structure assignment.

The cycloaddition of three-membered ring heterocycles with heterocumulenes has been the subject of many publications. There are examples of uncatalyzed reactions including that of oxaziridines with phenyl isothiocyanate, which affords thiadiazolidine thiones,[1] and the [4 + 2] cycloaddition of 1-azirines and thiobenzoyl isocyanate.[2] Organoantimony halides are capable of catalyzing cycloaddition of aziridines with carbon dioxide, carbon disulfide, and phenyl isothiocyanate usually forming five-membered heterocycles.[3,4] Either organotin[5] or organoantimony[6] halides catalyze cycloaddition of oxiranes and heterocumulenes.

In connection with our research on transition complex catalyzed ring expansion reactions of three-membered ring heterocycles[7,8] we examined the metal-catalyzed reaction of aziridines with carbodiimides, a process which, to our knowledge, does not occur in the absence of a metal catalyst. We now wish to report that use of an appropriate palladium(II) catalyst for the aziridine–carbodiimide reaction results in the regiospecific formation of imidazolidinimines in good to excellent yields.

Results and Discussion

Treatment of 1-*tert*-butyl-2-phenylaziridine (**1**, R = Ph, R′ = $C(CH_3)_3$) with diphenylcarbodiimide (**2**, Ar = Ph) in toluene at 100 °C and 5 psi nitrogen (glass autoclave), using catalytic quantities of tetrakis(triphenylphosphine)palladium(0), or bis(dibenzylideneacetone)palladium(0), with or without 2 equiv of benzonitrile (relative to palladium) resulted in complete recovery of the aziridine. However, if bis(benzonitrile)palladium dichloride is used as the catalyst, then clean reaction occurs affording the imidazolidenimine **3** in an isolated yield of 95%. The ratio of **1**/**2**/palladium catalyst used was 10:10:1. The reaction is sensitive to the nature of the nitrile ligand in the palladium catalyst. Use of acetonitrile, which is more basic than benzonitrile, as the nitrile ligand in the palladium catalyst in the reaction of the aziridine with diphenylcarbodiimide afforded **3** (R = Ph, R′ = $C(CH_3)_3$, Ar = Ph) in only 48% yield. The $(PhCN)_2PdCl_2$-catalyzed cycloaddition reaction was effected using different aziridines and either diphenyl or di-*p*-tolylcarbodiimide affording imidazolidinimines in 40–94% yields (see Table I for data).



The palladium(II)-catalyzed process proceeds in a regiospecific manner, with the aziridine reacting by cleavage of the more substituted ring carbon–nitrogen bond. The structure of **3** was elucidated on the basis of spectral data (Table I) as well as an X-ray analysis of **3** (R = p-BrC_6H_4,

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Table I. Reaction of Aziridines with Carbodiimides Catalyzed by (PhCN)$_2$PdCl$_2$[a]

1, R =, R^1 =	2, Ar =	3[b] (%)	IR, $\nu_{C=N}$ (cm^{-1})	MS (M)$^+$ (*m/e*)	NMR, (δ, ppm)	
					^{1}H	^{13}C
Ph, C(CH$_3$)$_3$	Ph	95[c]	1641	369	1.55 (s, 9 H, C(CH$_3$)$_3$), 3.31 (dd, 1 H, CH$_2$ *J* = 7.8, 8.7 Hz), 3.89 (t, 1 H, CH$_2$, *J* = 7.8, 8.7 Hz), 3.89 (t, 1 H, CH$_2$, *J* = 8.5 Hz), 4.53 (t, 1 H, CHPh, *J* = 7.9 Hz], 6.45–7.43 (m, 15 H, Ph)	27.14 (CH$_3$), 51.83 (CH$_2$), 54.36 (*C*(CH$_3$)$_3$), 65.66 (CHPh), 119.27, 122.17, 124.62, 125.56, 127.20, 127.76, 128.01, 128.80, 128.91 (CH-aromatic), 142.14, 143.54, 149.67 (quaternary aromatic carbons), 152.13 (C=N)
Ph, C(CH$_3$)$_3$	*p*-tolyl	80	1644	397	1.55 (s, 9 H, C(CH$_3$)$_3$), 2.06 (s, 3 H, CH$_3$), 2.08 (s, 3 H, CH$_3$), 3.29 (dd, 1 H, CH$_2$, *J* = 8.0, 8.8 Hz), 3.88 (t, 1 H, CH$_2$, *J* = 8.3 Hz), 4.52 (t, 1 H, CHPh, *J* = 7.9 Hz), 6.50–7.44 (m, 13 H, aromatic ring protons)	20.36, 20.59 (*p*-*C*H$_3$C$_6$H$_4$), 27.15 (CH$_3$), 51.82 (CH$_2$), 54.30 (*C*(CH$_3$)$_3$), 65.87 (CHPh), 122.01, 125.52, 127.27, 127.95, 128.24, 128.56, 128.71, 134.10, 141.25, 142.24, 147.03 (aromatic), 152.27 (C=N)
Ph, 1-adamantyl	Ph	94	1639	447	1.66–2.52 (m, 15 H, adamantyl), 3.42 (dd, 1 H, CH$_2$, *J* = 7.4, 8.7 Hz), 3.94 (t, 1 H, CH$_2$, *J* = 8.6 Hz), 4.51 (t, 1 H, CHPh, *J* = 7.7 Hz), 6.48–7.48 (m, 15 H, Ph)	29.80, 36.67, 39.42 (CH, CH$_2$-adamantyl), 50.88 (CH$_2$), 55.46 (C-adamantyl), 65.87 (CHPh), 119.28, 122.39, 124.63, 125.49, 127.22, 127.93, 128.16, 128.97, 142.47, 143.76, 149.89 (aromatic carbons), 151.77 (C=N)
Ph, 1-adamantyl	*p*-tolyl	61	1641	475	1.59–2.45 (m, 15 H, adamantyl), 2.03 (s, 3 H, CH$_3$), 2.05 (s, 3 H, CH$_3$), 3.32 (dd, 1 H, CH$_2$, *J* = 8.0, 8.6 Hz), 3.84 (t, 1 H, CH$_2$, *J* = 8.6 Hz), 4.47 (t, 1 H, CHPh, *J* = 8.1 hz), 6.45–7.42 (m, 13 H, aromatic protons)	20.39, 20.59 (*p*-*C*H$_3$C$_6$H$_4$), 29.66, 36.54, 39.08 (CH, CH$_2$-adamantyl), 50.74 (CH$_2$), 55.33 (C-adamantyl), 65.96 (CHPh), 120.92, 121.92, 125.30, 127.16, 127.90, 128.24, 128.54, 128.70, 133.99, 141.31, 142.42, 147.11 (aromatic carbons), 152.02 (C=N)
p-PhC$_6$H$_4$, C(CH$_3$)$_3$	Ph	72	1642	445	1.64 (s, 9 H, C(CH$_3$)$_3$), 3.43 (dd, 1 H, CH$_2$, *J* = 7.7, 8.1 Hz), 3.98 (t, 1 H, CH$_2$, *J* = 8.4 Hz), 4.64 (t, 1 H, CHAr, *J* = 7.8 Hz), 6.51–7.69 (m, 19 H, aromatic protons)	27.27 (CH$_3$), 51.85 (CH$_2$), 54.43 (*C*(CH$_3$)$_3$), 65.44 (CHAr), 119.41, 122.35, 124.71, 125.60, 127.14, 127.56, 127.67, 127.85, 128.13, 128.93, 140.68, 141.02, 141.26, 143.63, 149.72 (aromatic carbons) 151.99 (C=N)
p-PhC$_6$H$_4$, C(CH$_3$)$_3$	*p*-tolyl	62	1644	473	1.65 (s, 9 H, C(CH$_3$)$_3$), 2.14 (s, 3 H, CH$_3$), 2.15 (s, 3 H, CH$_3$), 3.40 (dd, 1 H, CH$_2$, *J* = 7.5, 9.2 Hz), 3.96 (t, 1 H, CH$_2$, *J* = 8.4 Hz), 4.63 (t, 1 H, CHAr, *J* = 8.0 Hz), 6.63–7.70 (m, 17 H, aromatic protons)	20.36, 20.56 (*p*-*C*H$_3$C$_6$H$_4$), 27.14 (CH$_3$), 51.82 (CH$_2$), 54.34 (*C*(CH$_3$)$_3$), 65.58 (CHAr), 122.01, 125.55, 127.08, 127.44, 127.70, 128.27, 128.62, 128.84, 134.16, 140.67, 140.87, 141.23, 146.99 (aromatic carbons), 152.36 (C=N)
p-PhC$_6$H$_4$, 1-adamantyl	Ph	71	1638	523	1.70–2.61 (m, 15 H, adamantyl), 3.51 (dd, 1 H, CH$_2$, *J* = 7.5, 8.3 Hz), 4.01 (t, 1 H, CH$_2$, *J* = 8.6 Hz), 4.67 (t, 1 H, CHAr, *J* = 7.7 Hz), 6.57–7.74 (m, 19 H, aromatic)	29.77, 36.63, 39.24 (CH, CH$_2$-adamantyl), 50.82 (CH$_2$), 55.49 (C-adamantyl), 65.53 (CHAr), 119.31, 122.38, 124.64, 125.48, 127.20, 127.63, 127.95, 128.19, 129.01, 140.73, 141.00, 141.51, 143.73, 149.86 (aromatic carbons), 151.73 (C=N)
p-PhC$_6$H$_4$, 1-adamantyl	*p*-tolyl	40	1640	551	1.53–2.40 (m, 15 H, adamantyl), 2.01 (s, 3 H, CH$_3$), 2.04 (s, 3 H, CH$_3$), 3.35 (dd, 1 H, CH$_2$, *J* = 7.5, 8.5 Hz), 3.8 (t, 1 H, CH$_2$, *J* = 8.7 Hz), 4.52 (t, 1 H, CHAr, *J* = 7.6 Hz), 6.52–7.60 (m, 17 H, aromatic)	20.39, 20.58 (*p*-*C*H$_3$C$_6$H$_4$), 29.67, 36.54, 39.10 (CH, CH$_2$-adamantyl), 50.72 (CH$_2$), 55.37 (C-adamantyl), 65.68 (CHAr), 121.98, 125.33, 127.10, 127.44, 127.61, 128.31, 128.63, 128.88, 134.03, 140.71, 140.80, 141.32, 141.45, 147.08 (aromatic carbons), 151.97 (C=N)
p-BrC$_6$H$_4$, C(CH$_3$)$_3$	Ph	90	1642	449, 447	1.52 (s, 9 H, C(CH$_3$)$_3$), 3.27 (dd, 1 H, CH$_2$, *J* = 7.5, 8.9 Hz), 3.91 (t, 1 H, CH$_2$, *J* = 8.6 Hz), 4.51 (t, 1 H, CHAr, *J* = 7.8 Hz), 6.44–7.53 (m, 14 H, aromatic)	27.11 (CH$_3$), 51.59 (CH$_2$), 54.40 (*C*(CH$_3$)$_3$), 65.11 (CHAr), 119.43, 121.91, 122.21, 124.85, 125.64, 127.77, 128.11, 128.89, 131.95, 141.07, 143.30, 149.43 (aromatic carbons), 151.75 (C=N)
p-BrC$_6$H$_4$, C(CH$_3$)$_3$	*p*-tolyl	78	1645	475, 477	1.51 (s, 9 H, C(CH$_3$)$_3$), 2.03 (s, 3 H, CH$_3$), 2.05 (s, 3 H, CH$_3$), 3.19 (dd, 1 H, CH$_2$, *J* = 8.0, 8.4 Hz), 3.82 (t, 1 H, CH$_2$, *J* = 8.4 Hz), 4.44 (t, 1 H, CHAr, *J* = 8.0 Hz), 6.41–7.50 (m, 12 H, aromatic)	20.42, 20.61 (*p*-*C*H$_3$C$_6$H$_4$), 27.15 (CH$_3$), 51.63 (CH$_2$), 54.37 (*C*(CH$_3$)$_3$), 65.34, (CHAr), 121.84, 122.02, 125.66, 128.31, 128.71, 129.04, 131.89, 134.42, 141.01, 141.16, 146.83 (aromatic carbons), 152.07 (C=N)

Table I (Continued)

1, R =, R^1 =	2, Ar =	3^b (%)	IR, $\nu_{C=N}$ (cm^{-1})	MS (M)$^+$ (*m*/*e*)	NMR, (δ, ppm)	
					^{1}H	^{13}C
Ph, *n*-C_4H_9	Ph	86	1640	369	0.89 (t, 3 H, CH_3), 1.29 (q, 2 H, CH_2CH_3), 1.54 (m, 2 H, $CH_2CH_2CH_3$), 3.29 (m, 3 H, NCH_2 and one H of CH_2 (ring)), 3.94 (t, 1 H, CH_2 ring, *J* = 8.8 Hz), 4.80 (dd, 1 H, *C*HPh, *J* = 8.5, 6.2 Hz), 6.58–7.43 (m, 15 H, aromatic)	13.94 (CH_3), 20.06, 29.20 (CH_3 CH_2CH_2), 46.08 (NCH_2), 54.22 (CH_2 ring), 64.61 (*CH*Ph), 120.07, 122.41, 124.11, 124.16, 126.73, 128.04, 128.10, 128.93, 141.98, 142.07, 149.15 (aromatic carbons), 151.91 (C=N)

[a] Reaction conditions: 1 (1.0 mmol), 2 (1.0 mmol), $(PhCN)_2PdCl_2$ (0.1 mmol), $PhCH_3$ (7.0 mL), 100 °C, 24 h, 5 psi N_2. Melting points and elemental analyses of 3 are given in the Experimental Section. [b] Isolated yields of pure materials. [c] 48% yield using $(CH_3CN_2)PdCl_2$.

Table II. Data Collection and Refinement

formula	$C_{25}H_{26}BrN_3$
cryst. system	triclinic
space group	p^{-1}
a, Å	12.953 (4)
b, Å	18.216 (10)
c, Å	10.121 (10)
α, deg	99.36 (7)
β, deg	91.084 (6)
γ, deg	72.50 (3)
V, Å^3	2247.0
FW	448.40
cryst size, mm	0.30 × 0.30 × 0.30 mm
d(calcd), g cm^3	1.326
total no. of reflns	7003
unique reflns	6660
obsd reflns^b	2679
no. of variables	316
final $R_F{}^c$	0.072^d
final $R_{WF}{}^e$	0.031^d
final GOF	3.54^d

[a] Rigaku diffractometer with MoKα radiation, λ of radiation = 0.7093 Å, $\theta - 2\theta$ scan mode, 2θ range of 0–47; Z = 4. [b] Reflection with $I > 2.5\ (\sigma(I))$. [c] $R_F = \sum||F_o| - |F_c|/|F_o|$. [d] Observed reflections only. [e] $R_{WF} = [\sum w(|F_o| - |F_c|)^2/\sum F_o{}^2]^{1/2}$. [f] $GOF = [\sum w(|F_o| - |F_c|)^2/(\text{no., of obs, – no. of vars})]$.

Table III. Atomic Parameters *x*, *y*, *z*, and B_{iso} for the Non-Hydrogen Atoms of 3 (R = *p*-BrC_6H_4, R = $C(CH_3)_3$, Ar = Ph) (molecule 1)^a

	x	*y*	*z*	B_{iso}
Br1	0.009 77 (12)	0.565 50 (9)	0.366 09 (15)	6.63 (10)
N1	0.3361 (7)	0.8240 (4)	0.2656 (7)	4.0 (6)
N2	0.4340 (6)	0.7254 (4)	0.3617 (7)	3.0 (5)
N3	0.4128 (6)	0.8592 (4)	0.4677 (7)	3.2 (6)
C1	0.3970 (8)	0.8064 (5)	0.3748 (9)	2.8 (7)
C2	0.3866 (8)	0.6912 (5)	0.2446 (9)	3.4 (7)
C3	0.3493 (8)	0.7560 (6)	0.1643 (9)	3.6 (7)
C22	0.2733 (8)	0.9033 (5)	0.2491 (9)	3.6 (7)
C23	0.3469 (9)	0.9530 (6)	0.2319 (11)	7.0 (10)
C24	0.1942 (9)	0.9426 (7)	0.3629 (10)	7.3 (9)
C25	0.2094 (10)	0.9043 (6)	0.1190 (11)	7.4 (10)
C4	0.4487 (6)	0.8443 (4)	0.5941 (4)	2.9 (3)
C5	0.5294 (6)	0.8757 (4)	0.6470 (8)	3.8 (3)
C6	0.5616 (5)	0.8694 (4)	0.7781 (8)	4.4 (3)
C7	0.5132 (6)	0.8316 (4)	0.8562 (4)	5.4 (3)
C8	0.4324 (6)	0.8003 (4)	0.8033 (8)	5.4 (3)
C9	0.4002 (4)	0.8066 (4)	0.6723 (8)	4.0 (3)
C10	0.5327 (5)	0.6807 (4)	0.4108 (6)	2.7 (3)
C11	0.6214 (7)	0.7089 (3)	0.4347 (6)	4.1 (3)
C12	0.7166 (5)	0.6624 (5)	0.4821 (7)	5.1 (3)
C13	0.7230 (5)	0.5878 (5)	0.5056 (6)	6.2 (3)
C14	0.6343 (8)	0.5596 (3)	0.4816 (7)	5.5 (3)
C15	0.5392 (6)	0.6061 (5)	0.4342 (7)	4.4 (3)
C16	0.2957 (4)	0.6597 (4)	0.2793 (8)	3.2 (3)
C17	0.2456 (6)	0.6787 (3)	0.4063 (6)	4.1 (3)
C18	0.1601 (6)	0.6505 (4)	0.4312 (5)	4.8 (3)
C19	0.1247 (4)	0.6035 (4)	0.3291 (9)	4.4 (3)
C20	0.1748 (6)	0.5845 (3)	0.2021 (7)	4.7 (3)
C21	0.2603 (6)	0.6126 (4)	0.1772 (5)	4.2 (3)

[b] B_{iso} is the mean of the principal axes of the thermal ellipsoid.

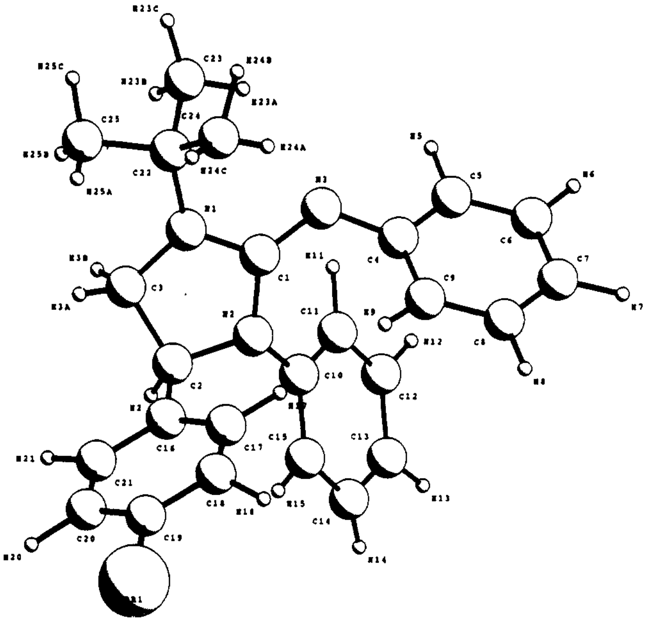


Figure 1. View of 3 (R = *p*-BrC_6H_4, R′ = $C(CH_3)_3$, Ar = Ph (molecule 1) showing the atom numbering scheme.

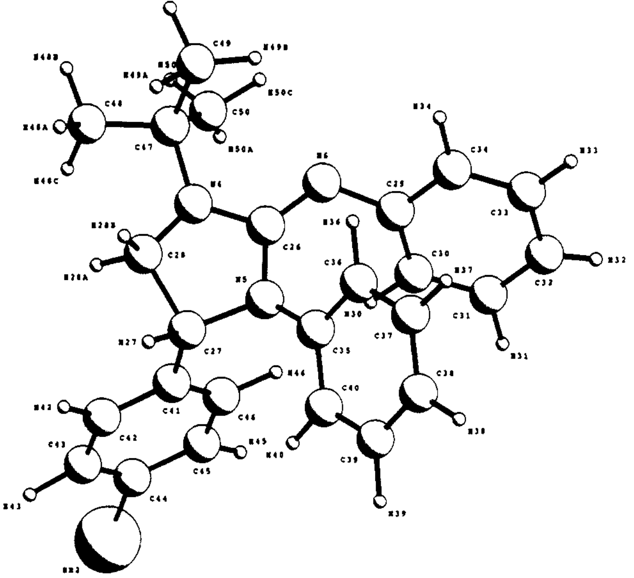


Figure 2. View of 3 (R = *p*-BrC_6H_4, R′ = $C(CH_3)_3$, Ar = Ph (molecule 2) showing the atom numbering scheme.

R′ = $C(CH_3)_3$, Ar = Ph). The imine stretching absorption of 3 occurred in the infrared spectrum at 1638–1645 cm^{-1}. An abundant molecular ion peak appeared in the mass spectrum of all of the products. The proton and carbon magnetic resonance spectra were consistent with the assigned structure, one characteristic signal being that of the

Table IV. Selected Interatomic Distances (Å) and Angles (deg) of 3 (R = *p*-BrC_6H_4, R′ = $C(CH_3)_3$, Ar = Ph) (molecule 1)

	Bond Distances		
Br(1)–C(19)	1.886 (8)	C(5)–H(5)	1.077 (8)
N(1)–C(1)	1.369 (11)	C(6)–C(7)	1.395 (12)
N(1)–C(3)	1.444 (12)	C(6)–H(6)	1.080 (7)
N(1)–C(22)	1.464 (12)	C(7)–C(8)	1.395 (12)
N(2)–C(1)	1.392 (12)	C(7)–H(7)	1.122 (5)
N(2)–C(2)	1.461 (12)	C(8)–C(9)	1.395 (11)
N(2)–C(10)	1.424 (9)	C(8)–H(8)	1.083 (8)
N(3)–C(1)	1.294 (11)	C(9)–H(9)	1.089 (7)
N(3)–C(4)	1.393 (9)	C(10)–C(11)	1.395 (12)
C(2)–C(3)	1.496 (13)	C(10)–C(15)	1.395 (12)
C(2)–C(16)	1.525 (12)	C(11)–C(12)	1.395 (10)
C(2)–H(2)	1.065 (9)	C(11)–H(11)	1.082 (6)
C(3)–H(3A)	1.099 (10)	C(12)–C(13)	1.395 (13)
C(3)–H(3B)	1.094 (9)	C(12)–H(12)	1.077 (8)
C(22)–C(23)	1.529 (14)	C(13)–C(14)	1.395 (13)
C(22)–C(24)	1.491 (14)	C(13)–H(13)	1.104 (6)
C(22)–C(25)	1.542 (14)	C(14)–C(15)	1.395 (10)
C(23)–H(23A)	0.99 (7)	C(14)–H(14)	0.90 (8)
C(23)–H(23B)	1.135 (12)	C(15)–H(15)	1.066 (9)
C(23)–H(23C)	1.033 (10)	C(16)–C(17)	1.395 (10)
C(24)–H(24B)	1.121 (12)	C(16)–C(21)	1.395 (10)
C(24)–H(24C)	1.057 (11)	C(17)–C(18)	1.395 (12)
C(25)–H(25A)	1.070 (12)	C(17)–C(17)	1.066 (7)
C(25)–H(25B)	0.71 (6)	C(18)–C(19)	1.395 (10)
C(25)–H(25C)	1.061 (11)	C(18)–H(18)	1.05 (6)
C(4)–C(5)	1.395 (11)	C(19)–C(20)	1.395 (11)
C(4)–C(9)	1.395 (11)	C(20)–C(21)	1.395 (12)
C(5)–C(6)	1.395 (11)	C(20)–H(20)	1.111 (7)
		C(21)–H(21)	1.097 (5)
	Bond Angles		
C(1)–N(1)–C(3)	111.7 (7)	C(7)–C(6)–H(6)	120.3 (7)
C(1)–N(1)–C(22)	123.8 (7)	C(6)–C(7)–C(8)	120.0 (6)
C(3)–N(1)–C(22)	124.3 (7)	C(6)–C(7)–H(7)	120.1 (8)
C(1)–N(2)–C(2)	109.5 (7)	C(8)–C(7)–H(7)	119.9 (7)
C(1)–N(2)–C(10)	126.0 (7)	C(7)–C(8)–C(9)	120.0 (7)
C(2)–N(2)–C(10)	119.6 (7)	C(7)–C(8)–H(8)	119.9 (7)
C(1)–N(3)–C(4)	123.1 (7)	C(9)–C(8)–H(8)	120.1 (7)
N(1)–C(1)–N(2)	107.0 (7)	C(4)–C(9)–C(8)	120.0 (6)
N(1)–C(1)–N(3)	122.8 (8)	C(4)–C(9)–H(9)	118.9 (7)
N(2)–C(1)–N(3)	130.2 (8)	C(8)–C(9)–H(9)	120.6 (8)
N(2)–C(2)–C(3)	103.7 (7)	N(2)–C(10)–C(11)	122.3 (7)
N(2)–C(2)–C(16)	113.6 (7)	N(2)–C(10)–C(15)	117.7 (7)
N(2)–C(2)–H(2)	109.7 (8)	C(11)–C(10)–C(15)	120.0 (6)
C(3)–C(2)–C(16)	112.8 (8)	C(10)–C(11)–C(12)	120.0 (7)
C(3)–C(2)–H(2)	108.6 (8)	C(10)–C(11)–H(11)	120.3 (7)
C(16)–C(2)–H(2)	108.1 (7)	C(12)–C(11)–H(11)	119.7 (9)
N(1)–C(3)–C(2)	101.9 (7)	C(11)–C(12)–C(13)	120.0 (7)
N(1)–C(3)–H(3A)	113.7 (8)	C(11)–C(12)–H(12)	119.5 (9)
N(1)–C(3)–H(3B)	111.8 (8)	C(13)–C(12)–H(12)	120.5 (6)
C(2)–C(3)–H(3A)	110.7 (8)	C(12)–C(13)–C(14)	120.0 (6)
C(2)–C(3)–H(3B)	111.7 (8)	C(12)–C(13)–H(13)	115.5 (7)
H(3A)–C(3)–H(3B)	107.0 (7)	C(14)–C(13)–H(13)	124.5 (8)
N(1)–C(22)–C(23)	111.5 (8)	C(13)–C(14)–C(15)	120.0 (7)
N(1)–C(22)–C(24)	112.1 (8)	C(13)–C(14)–H(14)	93 (5)
N(1)–C(22)–C(25)	111.9 (8)	C(15)–C(14)–H(14)	145 (5)
C(23)–C(22)–C(24)	109.9 (8)	C(10)–C(15)–C(14)	120.0 (7)
C(23)–C(22)–C(25)	103.4 (8)	C(10)–C(15)–H(15)	120.8 (6)
C(24)–C(22)–C(25)	107.7 (9)	C(14)–C(15)–H(15)	119.2 (8)
C(22)–C(23)–H(23A)	96 (4)	C(2)–C(16)–C(17)	122.4 (7)
C(22)–C(23)–H(23B)	110.1 (9)	C(2)–C(16)–C(21)	117.5 (7)
C(22)–C(23)–H(23C)	117.7 (10)	C(17)–C(16)–C(21)	120.0 (7)
H(23A)–C(23)–H(23B)	107 (4)	C(16)–C(17)–C(18)	120.0 (6)
H(23A)–C(23)–H(23C)	115 (4)	C(16)–C(17)–H(17)	119.9 (7)
H(23B)–C(23)–H(23C)	108.7 (9)	C(18)–C(17)–H(17)	120.1 (6)
C(22)–C(24)–H(24A)	95 (4)	C(17)–C(18)–C(19)	120.0 (6)
C(22)–C(24)–H(24B)	111.9 (10)	C(17)–C(18)–H(18)	121 (4)
C(22)–C(24)–H(24C)	115.5 (9)	C(19)–C(18)–H(18)	113 (4)
H(24A)–C(24)–H(24B)	87 (4)	Br(1)–C(19)–C(18)	119.1 (6)
H(24A)–C(24)–H(24C)	135 (5)	Br(1)–C(19)–C(20)	120.9 (6)
H(24B)–C(24)–H(24C)	108.1 (9)	C(18)–C(19)–C(20)	120.0 (7)
C(22)–C(25)–H(25A)	102.8 (9)	C(19)–C(20)–C(21)	120.0 (6)
C(22)–C(25)–H(25B)	104 (5)	C(19)–C(20)–H(20)	118.8 (7)
C(22)–C(25)–H(25C)	108.2 (9)	C(21)–C(20)–H(20)	121.1 (6)
H(25A)–C(25)–H(25B)	116 (5)	C(16)–C(21)–C(20)	120.0 (6)
H(25A)–C(25)–H(25C)	108.8 (10)	C(16)–C(21)–H(21)	122.9 (8)
H(25B)–C(25)–H(25C)	115 (5)	C(20)–C(21)–H(21)	117.1 (6)
N(3)–C(4)–C(5)	117.1 (7)		
N(3)–C(4)–C(9)	122.6 (7)		
C(5)–C(4)–C(9)	120.0 (6)		
C(4)–C(5)–C(6)	120.0 (7)		
C(4)–C(5)–H(5)	119.7 (7)		
C(6)–C(5)–H(5)	120.3 (7)		
C(5)–C(6)–C(7)	120.0 (7)		
C(5)–C(6)–H(6)	119.7 (8)		

Table V. Atomic Parameters *x*, *y*, *z*, and B_{iso} for the Non-Hydrogen Atoms of 3 (R = *p*-BrC_6H_4, R′ = $C(CH_3)_3$, Ar = Ph (molecule 2)[a]

	x	*y*	*z*	B_{iso}
Br2	−0.495 52 (12)	0.567 63 (9)	0.862 75 (15)	6.80 (10)
N4	−0.1849 (7)	0.8290 (4)	1.1311 (7)	3.9 (6)
N5	−0.0783 (6)	0.7334 (4)	0.9814 (7)	2.9 (5)
N6	−0.1124 (7)	0.8679 (4)	0.9545 (7)	4.5 (7)
C26	−0.1210 (8)	0.8137 (5)	1.0160 (9)	3.1 (7)
C27	−0.1173 (8)	0.6915 (5)	1.0773 (8)	3.2 (7)
C28	−0.1578 (8)	0.7605 (6)	1.1946 (9)	3.4 (7)
C47	−0.2415 (8)	0.9090 (5)	1.2043 (9)	3.8 (7)
C48	−0.3039 (9)	0.9027 (6)	1.3225 (9)	5.5 (8)
C49	−0.1598 (9)	0.9520 (6)	1.2489 (10)	6.8 (9)
C50	−0.3164 (9)	0.9533 (6)	1.1108 (10)	6.3 (9)
C29	−0.0710 (6)	0.8528 (4)	0.8214 (5)	3.4 (3)
C30	−0.1129 (5)	0.8111 (4)	0.7175 (9)	4.1 (3)
C31	−0.0761 (6)	0.8033 (4)	0.5858 (7)	5.2 (3)
C32	0.0026 (7)	0.8372 (4)	0.5580 (5)	5.7 (3)
C33	0.0446 (5)	0.8789 (4)	0.6619 (9)	4.6 (3)
C34	0.0078 (6)	0.8867 (3)	0.7936 (7)	4.4 (3)
C35	0.0217 (4)	0.6943 (4)	0.9163 (6)	3.8 (3)
C36	0.1037 (7)	0.7295 (3)	0.9171 (6)	3.9 (3)
C37	0.2017 (5)	0.6893 (5)	0.8480 (7)	5.1 (4)
C38	0.2177 (5)	0.6140 (5)	0.7780 (6)	5.4 (3)
C39	0.1356 (7)	0.5789 (3)	0.7772 (6)	5.5 (3)
C40	0.0376 (6)	0.6191 (5)	0.8464 (7)	4.4 (3)
C41	−0.2090 (4)	0.6613 (4)	1.0165 (8)	3.0 (3)
C42	−0.2486 (6)	0.6185 (4)	1.0944 (5)	4.1 (3)
C43	−0.3336 (6)	0.5897 (3)	1.0493 (8)	4.7 (3)
C44	−0.3790 (4)	0.6037 (4)	0.9263 (8)	4.2 (3)
C45	−0.3395 (6)	0.6465 (4)	0.8484 (5)	4.8 (3)
C46	−0.2545 (6)	0.6753 (3)	0.8935 (7)	4.5 (3)

[a] B_{iso} is the mean of the principal axes of the thermal ellipsoid.

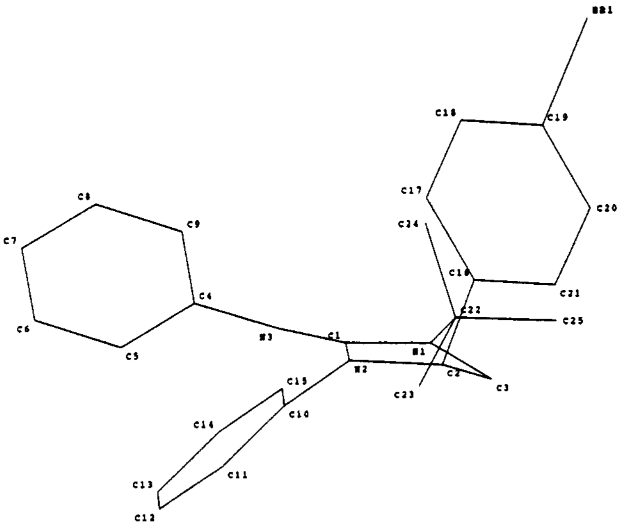


Figure 3. Representation of 3 (R = *p*-BrC_6H_4, R′ = $C(CH_3)_3$, Ar = Ph) (molecule 1) showing the relationship between substituent groups.

imine carbon which appeared at δ 151.73–152.36. Note that the three heterocyclic ring protons usually appear as a doublet of doublets and two triplets, the latter probably a result of overlapping doublets in each case.

The structure of 3 (R = *p*-BrC_6H_4, R′ = $C(CH_3)_3$, Ar = Ph) in the solid state shows some interesting features. There are two different molecules in the asymmetric unit (data collection information, atomic coordinates, and selected interatomic distances and angles are listed in Tables II–VI). Views of the two different molecules (denoted as 3(1) and 3(2)) are given in Figures 1 and 2. The difference between the two can be seen by examination of Figures 3 and 4 which reveal that the torsion angles are not the

Table VI. Selected Interatomic Distances (Å) and Angles (deg) of 3 ($R = p\text{-}BrC_6H_4$, $R' = C(CH_3)_3$, Ar = Ph) (molecule 2)

Bond Distances

Br(2)–C(44)	1.883 (7)	C(30)–H(30)	1.078 (7)
N(4)–C(26)	1.383 (12)	C(31)–C(32)	1.395 (13)
N(4)–C(28)	1.443 (12)	C(31)–H(31)	1.088 (7)
N(4)–C(47)	1.496 (12)	C(32–C(33)	1.395 (11)
N(5)–C(26)	1.386 (11)	C(32)–H(32)	0.98 (7)
N(5)–C(27)	1.507 (11)	C(33–C(34)	1.395 (12)
N(5)–C(35)	1.394 (9)	C(33)–H(33)	1.072 (8)
N(6)–C(26)	1.282 (12)	C(34)–H(34)	1.087 (7)
N(6)–C(29)	1.413 (9)	C(35)–C(36)	1.395 (11)
C(27)–C(28)	1.551 (13)	C(35)–C(40)	1.395 (11)
C(27)–C(41)	1.534 (12)	C(36)–C(37)	1.395 (10)
C(27)–H(27)	1.30 (6)	C(36)–H(36)	1.079 (5)
C(28)–H(28A)	1.072 (10)	C(37)–C(38)	1.395 (11)
C(28)–H(28B)	1.18 (7)	C(37)–H(37)	1.069 (9)
C(47)–C(48)	1.495 (14)	C(38)–C(39)	1.395 (12)
C(47)–C(49)	1.518 (14)	C(38)–H(38)	1.099 (5)
C(47)–C(50)	1.494 (14)	C(39)–C(40)	1.395 (10)
C(48)–H(48A)	1.18 (6)	C(39)–H(39)	1.123 (5)
C(48)–H(48B)	1.077 (10)	C(40)–H(40)	1.080 (9)
C(48)–H(48C)	1.122 (11)	C(41)–C(42)	1.395 (11)
C(49)–H(49A)	1.09 (6)	C(41)–C(46)	1.395 (11)
C(49)–H(49B)	1.069 (11)	C(42)–C(43)	1.395 (12)
C(49)–H(49C)	1.069 (10)	C(42)–H(42)	1.083 (5)
C(50)–H(50A)	0.70 (7)	C(43)–C(44)	1.395 (11)
C(50)–H(50B)	1.127 (11)	C(43)–H(43)	1.102 (8)
C(50)–H(50C)	1.063 (11)	C(44)–C(45)	1.395 (12)
C(29)–C(30)	1.395 (10)	C(45)–C(46)	1.395 (12)
C(29)–C(34)	1.395 (12)	C(45)–H(45)	1.110 (6)
C(30)–C(31)	1.395 (12)	C(46)–H(46)	1.075 (8)

Bond Angles

C(26)–N(4)–C(28)	109.2 (7)	C(30)–C(31)–H(31)	120.3 (8)
C(26)–N(4)–C(47)	124.5 (7)	C(32)–C(31)–H(31)	119.7 (6)
C(28)–N(4)–C(47)	122.8 (7)	C(31)–C(32)–C(33)	120.0 (6)
C(26)–N(5)–C(27)	111.4 (7)	C(31)–C(32)–H(32)	115 (4)
C(26)–N(5)–C(35)	125.4 (7)	C(33)–C(32)–H(32	120 (4)
C(27)–N(5)–C(35)	116.5 (7)	C(32)–C(33)–C(34)	120.0 (7)
C(26)–N(6)–C(29)	122.5 (8)	C(32)–C(33)–H(33)	119.3 (8)
N(4)–C(26)–N(5)	108.0 (7)	C(34)–C(33)–H(33)	120.6 (7)
N(4)–C(26)–N(6)	122.3 (8)	C(29)–C(34)–C(33)	120.0 (6)
N(5)–C(26)–N(6)	129.6 (8)	C(29)–C(34)–H(34)	121.3 (6)
N(5)–C(27)–C(28)	98.8 (7)	C(33)–C(34)–H(34)	118.6 (7)
N(5)–C(27)–C(41)	110.4 (7)	N(5)–C(35)–C(36)	121.6 (6)
N(5)–C(27)–H(27)	126 (3)	N(5)–C(35)–C(40)	118.4 (7)
C(28)–C(27)–C(41)	112.5 (7)	C(36)–C(35)–C(40)	120.0 (5)
C(28)–C(27)–H(27)	86.0 (24)	C(35)–C(36)–C(37)	120.0 (6)
C(41)–C(27)–H(27)	116 (3)	C(35)–C(36)–C(37)	120.0 (6)
N(4)–C(28)–C(27)	104.3 (7)	C(35)–C(36)–H(36)	120.1 (7)
N(4)–C(28)–H(28A)	107.4 (8)	C(37)–C(36)–H(36)	119.9 (8)
N(4)–C(28)–H(28B)	118 (3)	C(36)–C(37)–C(38)	120.0 (7)
C(27)–C(28)–H(28A)	106.2 (8)	C(36)–C(37)–H(37)	122.4 (7)
C(27)–C(28)–H(28B)	107 (3)	C(38)–C(37)–H(37)	117.6 (6)
H(28A)–C(28)–H(28B)	111 (3)	C(37)–C(38)–C(39)	120.0 (5)
N(4)–C(47)–C(48)	109.4 (8)	C(37)–C(38)–H(38)	121.2 (7)
N(4)–C(47)–C(49)	110.2 (8)	C(39)–C(38)–H(38)	118.8 (7)
N(4)–C(47)–C(50)	108.5 (7)	C(38)–C(39)–C(40)	120.0 (6)
		C(38)–C(39)–H(39)	118.8 (7)
C(48)–C(47)–C(49)	110.5 (8)		
C(48)–C(47)–C(50)	110.1 (9)	C(40)–C(39)–H(39)	121.1 (8)
C(49)–C(47)–C(50)	108.1 (8)	C(35)–C(40)–C(39)	120.0 (7)
C(47)–C(48)–H(48A)	108 (3)	C(35)–C(40)–H(40)	120.4 (6)
C(47)–C(48)–H(48B)	113.7 (9)	C(39)–C(40)–H(40)	119.6 (7)
C(47)–C(48)–H(48C)	112.2 (8)	C(27)–C(41)–C(42)	115.5 (7)
H(48A)–C(48)–H(48B)	101 (3)	C(27)–C(41)–C(46)	124.5 (7)
H(48A)–C(48)–H(48C)	114 (3)	C(42)–C(41)–C(46)	120.0 (6)
H(48B)–C(48)–H(48C)	106.6 (9)	C(41)–C(42)–C(43)	120.0 (6)
C(47)–C(49)–H(49A)	89 (4)	C(41)–C(42)–H(42)	120.1 (7)
C(47)–C(49)–H(49B)	114.2 (9)	C(43)–C(42)–H(42)	119.9 (7)
C(47)–C(49)–H(49C)	112.5 (9)	C(42)–C(43)–C(44)	120.0 (7)
H(49A)–C(49)–H(49B)	127 (4)	C(42)–C(43)–H(43)	121.2 (7)
H(49A)–C(49)–H(49C)	99 (4)	C(44)–C(43)–H(43)	118.7 (7)
H(49B)–C(49)–H(49C)	111.2 (10)	Br(2)–C(44)–C(43)	121.5 (6)
C(47)–C(50)–H(50A)	130 (5)	Br(2)–C(44)–C(45)	118.5 (6)
C(47)–C(50)–H(50B)	111.7 (8)	C(43)–C(44)–C(45)	120.0 (7)
C(47)–C(50)–H(50C)	117.1 (10)	C(44)–C(45)–C(46)	120.0 (6)
H(50A)–C(50)–H(50B)	91 (5)	C(44)–C(45)–H(45)	120.0 (7)
H(50A)–C(50)–H(50C)	94 (5)	C(46)–C(45)–H(45)	119.9 (7)
H(50B)–C(50)–H(50C)	107.2 (9)	C(41)–C(46)–C(45)	120.0 (7)
N(6)–C(29)–C(30)	121.9 (8)	C(41)–C(46)–H(46)	117.9 (7)
N(6)–C(29)–C(34)	117.9 (6)	C(45)–C(46)–H(46)	121.9 (7)
C(30)–C(29)–C(34)	120.0 (6)		
C(29)–C(30)–C(31)	120.0 (7)		
C(29)–C(30)–H(30)	119.2 (8)		
C(31)–C(30)–H(30)	120.6 (7)		
C(30)–C(31)–C(32)	120.0 (6)		

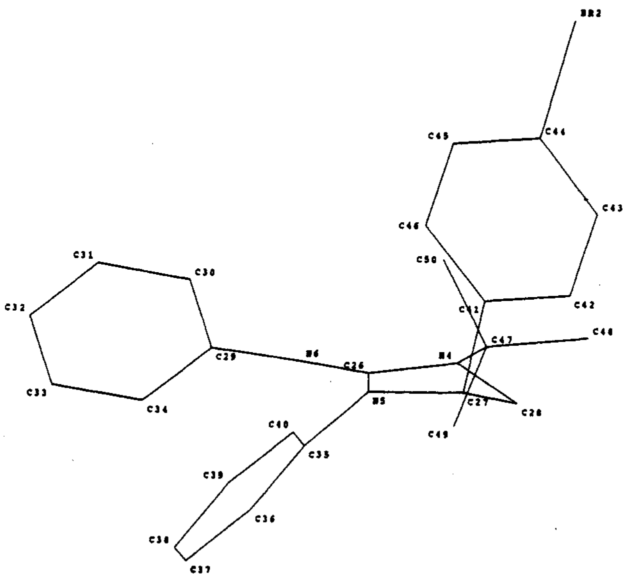
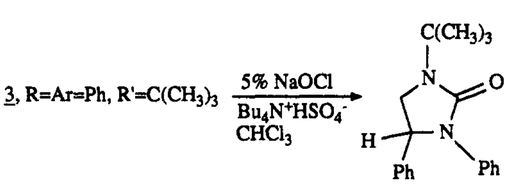


Figure 4. Representation of 3 ($R = p\text{-}BrC_6H_4$, $R' = C(CH_3)_3$, Ar = Ph) (molecule 2) showing the relationship between substituent groups.

same, especially when one considers the position of the *tert*-butyl group with respect to the *p*-bromophenyl unit. Specifically, the torsion angle for C(47)N(4)C(26)N(6) is 81.53° in molecule 3(2) compared with a torsion angle of −51.76° for the same series of atoms in 3(1). Similarly, the value is 54.35° for C(47)N(4)N(5)C(35) in 3(2) while the torsion angle is −78.33° for the corresponding atoms in 3(1). The phenyl group, attached to the imine nitrogen, is located anti to the N–$C(CH_3)_3$ unit (or syn to the N–Ph portion of the five-membered ring). The *p*-bromophenyl substituent is in a trans relationship with respect to the phenyl group attached to the saturated nitrogen atom and is cis with respect to the *tert*-butyl group in both molecules. As expected, the carbon–nitrogen double bond is shorter (1.282 Å) than the two single C–N bonds involving the same carbon atom in each molecule. The bond distances of the latter are not equivalent, and this is reflected in the different NCN bond angles.

The imidazolidenimine 3 (R = Ar = Ph, $R' = C(CH_3)_3$) can be hydrolyzed to the imidazolidinone 4 by treatment with 1 N HCl in toluene but the yield is only 5%. However, use of sodium hypochlorite as the reagent under phase transfer catalysis conditions gave 4 in 57% yield.



(4)

A possible mechanism for the palladium-catalyzed cycloaddition reaction is outlined in Scheme I. Interaction of $(PhCN)_2PdCl_2$ with the aziridine may afford the N-donor ligand complex 5. Reaction of the latter with the carbodiimide can form 6 in which there is π-complexation of one of the carbon–nitrogen double bonds to palladium. It is also conceivable that the sequence of complexation of the organic reactants to palladium is reversed (i.e.,

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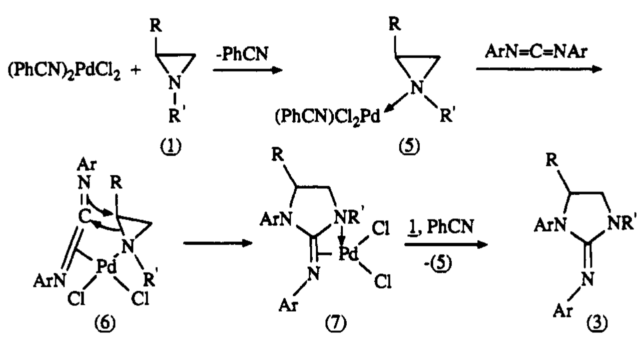
(9) Campbell, T. W.; Monagle, J. J. *Organic Syntheses*; Wiley, New York, 1973; Coll. Vol. V, p 501.

(10) Doyle, J. R.; Slade, P. E.; Jonassen, H. B. *Inorg. Synth.* **1960**, *6*, 218.

Scheme I



carbodiimide before aziridine), but the same intermediate **6** would result. It is also possible that the η- (lone pair) rather than π-electrons of the carbodiimide participate in bonding to palladium. Cycloaddition of the aziridine to the uncomplexed double bond of the carbodiimide ligand would give **7**. Reaction of the latter with additional aziridine and benzonitrile (previously dissociated from $(PhCN)_2PdCl_2$) could afford the imidazolidinimine and regenerate **5**.

In conclusion, bis(benzonitrile)palladium dichloride is an effective catalyst for the regiospecific cycloaddition of aziridines and carbodiimides under quite mild conditions.

Experimental Section

General. A Fisher-Johns apparatus was used for melting point determinations. The following spectrometers were used to obtain spectral data: Bomem MB100-C15 (FR-IR), Varian XL-300 and/or Gemini 200 (NMR), VG 7070E (MS). The aziridines were synthesized by known methods.[7] The carbodiimides and the palladium catalysts were either purchased or prepared according to literature procedures.[9,10] Organic solvents were dried and distilled prior to use. Elemental analyses were carried out by MHW Laboratories, Phoenix, AZ.

All reactions were conducted under a dry nitrogen atmosphere.

General Procedure for the Palladium-Catalyzed Cycloaddition Reaction of Aziridines with Carbodiimides. A mixture of aziridine (**1**, 1.0 mmol), carbodiimide (**2**, 1.0 mmol) and bis(benzonitrile)palladium dichloride (0.038 g, 0.10 mmol) in toluene (7.0 mL) was heated, with stirring, in a glass autoclave for 24 h at 100 °C (oil bath temperature) under a slight pressure of nitrogen (5 psi). After being cooled at room temperature, the autoclave was opened and the brown homogeneous solution was filtered through Celite. The filtrate was concentrated by rotary evaporation, and the crude product was purified by silica gel thin-layer chromatography using 25:1 toluene/acetonitrile as the developer.

Melting points, yields, and analytical data (see Table I for spectral results) for **3** are as follows: (a) R = Ph, R' = $C(CH_3)_3$, Ar = Ph; mp 88–90° C. Anal. Calcd for $C_{25}H_{27}N_3$: C, 81.26; H, 7.37; N, 11.37. Found: C, 80.82; H, 7.39; N, 11.35. (b) R = Ph, R' = $C(CH_3)_3$, Ar = *p*-tolyl: mp 103–105 °C. Anal. Calcd for $C_{27}H_{31}N_3$: C, 81.57; H, 7.86; N, 10.57. Found: C, 81.65; H, 7.67; N, 10.23. (c) R = Ph, R' = 1-$C_{10}H_{15}$, Ar = Ph: mp 120–121 °C. Anal. Calcd for $C_{31}H_{33}N_3$: C, 83.18; H, 7.43; N, 9.39. Found: C, 82.88; H, 7.54; N, 9.45. (d) R = Ph, R' = 1-$C_{10}H_{15}$, Ar = *p*-tolyl: mp 151–153 °C. Anal. Calcd for $C_{33}H_{37}N_3$: C, 83.32; H, 7.84; N, 8.83. Found: C, 83.22; H, 7.94; N, 8.85. (e) R = *p*-PhC_6H_4, R' = $C(CH_3)_3$, Ar = Ph; mp 108–109 °C. Anal. Calcd for $C_{31}H_{31}H_3$: C, 83.56; H, 7.01; N, 9.43. Found: C, 83.14; H, 6.94; N, 9.40. (f) R = *p*-PhC_6H_4, R' = $C(CH_3)_3$, Ar = *p*-tolyl: mp 133–135 °C. Anal. Calcd for $C_{33}H_{35}N_3$: C, 83.68; H, 7.45; N, 8.87. Found: C, 83.79; H, 7.41; N, 8.66. (g) R = *p*-PhC_6H_4, R' = 1-$C_{10}H_{15}$, Ar = Ph: mp 165–166 °C. Anal. Calcd for $C_{37}H_{37}N_3$: C, 84.85; H, 7.12; N, 8.02. Found: C, 84.52; H, 7.17; N, 7.79. (h) R = *p*-PhC_6H_4, R' = 1-$C_{10}H_{15}$, Ar = *p*-tolyl: mp 195–197 °C. Anal. Calcd for $C_{39}H_{41}N_3$: C, 84.89; H, 7.49; N, 7.62. Found: C, 85.06; H, 7.12; N, 7.30. (i) R = *p*-BrC_6H_4, R' = $C(CH_3)_3$, Ar = Ph: mp 143–145 °C. Anal. Calcd for $C_{25}H_{26}BrN_3$: C, 66.96; H, 5.95; N, 9.37. Found: C, 66.80; H, 5.92; N, 9.30. (j) R = *p*-BrC_6H_4, R' = $C(CH_3)_3$, Ar = *p*-tolyl: mp 166–168 °C. Anal. Calcd for $C_{27}H_{30}BrN_3$: C, 68.06; H, 6.35; N, 8.38. Found: C, 68.34; H, 6.04; N, 8.85. (k) R = Ph, R' = *n*-C_4H_9, Ar = Ph: mp 35–36 °C. Anal. Calcd for $C_{25}H_{27}N_3$: C, 81.26; H, 7.39; N, 11.37. Found: C, 81.04; H, 7.05; N, 11.55.

Hydrolysis of 3 (R = Ar = Ph, R' = $C(CH_3)_3$). A mixture of the imidazolidinimine (0.092 g, 0.25 mmol), 5% NaOCl (2.0 mL) and tetra-*n*-butylammonium hydrogen sulfate (0.017 g, 0.05 mmol) in chloroform (2.0 mL) was stirred for 18 h at room temperature under nitrogen. The organic phase was separated, washed with water, dried ($MgSO_4$), and concentrated by rotary evaporation. The crude product was purified by silica gel thin-layer chromatography using 25:1 toluene/acetonitrile as the developer affording **4** in 57% yield: IR ν(CO) 1676 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.46 (s, 9 H, $C(CH_3)_3$), 3.37 (t, 1 H, CH_2), 3.87 (t, 1 H, CH_2), 5.33 (t, 1 H, CHPh), 6.90–7.55 (m, 10 H, Ph); MS (*m/e*) 294 (M)$^+$.

X-ray Analysis. A plate crystal of $C_{25}H_{26}BrN_3$ was mounted on a glass capillary, and all measurements were made on a Rigaku diffractometer with MoKα radiation. Cell dimensions and the orientation matrix were obtained from least-squares refinement using the setting angles of 25 reflections in the range $30° < 2\theta < 47°$ corresponding to a triclinic cell with dimensions given in Table II. For $Z = 4$ and FW = 448.40, the calculated density is 1.326 g/cm^3. The space group was determined to be p^{-1}. The data was collected at 22°C using the $\omega - 2\theta$ scan technique to a maximum 2θ value of 47, and the data were collected for Lorentz and polarization effects.[11]

The structure was solved by direct methods. All of the atoms with the exception of hydrogen were refined anisotropically. The final cycle of full matrix least-squares refinement was based on 2679 observed reflections ($I > 2.5\ \sigma(I)$) and 316 variable parameters. All calculations were performed using the NRC VAX crystallographic software package.[12]

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Registry No. 1 (R = Ph, R' = $C(CH_3)_3$), 116780-44-0; 1 (R = Ph, R' = 1-adamantyl, 116670-37-2; 1 (R = *p*-PhC_6H_4, R' = $C(CH_3)_3$), 116670-38-3; 1 (R = *p*-PhC_{6-4}, R' = 1-adamantyl, 116670-39-4; 1 (R = *p*-BrC_6H_4, R' = $C(CH_3)_3$), 116670-40-7; 1 (R = Ph, R' = *n*-C_4H_9), 136912-53-3; 2 (Ar = Ph), 622-16-2; 2 (Ar = *p*-tolyl), 726-42-1; **3a** (R = Ph, R' = $C(CH_3)_3$, Ar = Ph), 136912-55-5; **3b** (R = Ph, R' = $C(CH_3)_3$, Ar = *p*-tolyl), 136912-55-5; **3c** (R = Ph, R' = 1-$C_{10}H_{15}$, Ar = Ph), 136912-56-6; **3d** (R = Ph, R' = 1-$C_{10}H_{15}$, Ar = *p*-tolyl), 136912-57-7; **3e** (R = *p*-PhC_6H_4, R' = $C(CH_3)_3$, Ar = Ph), 136912-58-8; **3f** (R = *p*-PhC_6H_4, R' = $C(CH_3)_3$, Ar = *p*-tolyl), 136912-59-9; **3g** (R = *p*-PhC_6H_4, R' = 1-$C_{10}H_{15}$, Ar = Ph), 136912-60-2; **3h** (R = *p*-PhC_6H_4, R' = $C_{10}H_{15}$, Ar = *p*-tolyl), 136912-61-3; **3i** (R = *p*-BrC_6H_4, R' = $C(CH_3)_3$, Ar = Ph), 136947-09-6; **3j** (R = *p*-BrC_6H_4, R' = $C(CH_3)_3$, Ar = *p*-tolyl), 136912-62-4; **3k** (R = Ph, R^1 = *n*-C_4H_9, Ar = Ph), 136912-63-5; 4, 136912-64-6; $PdCL_2(PhCN)_2$, 14220-64-5.

Supplementary Material Available: Tables of anisotropic temperature factors and torsion angles for **3**, R = *p*-BrC_6H_4, R' = $C(CH_3)_3$, Ar = Ph (4 pages). Ordering information is given on any current masthead page.

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