Synthesis of Nortricyclenes from Norbornadiene Using Palladium Complexes and Zinc Powder

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Norbornadiene reacts with aryl or benzyl halides in the presence of palladium complexes, zinc powder and water to give the corresponding substituted nortricyclenes in good yields.

Although scattered reports on the synthesis of substituted nortricyclenes have appeared, there is still no general efficient method for preparing these compounds, particularly with carbon substituents.^{1–5} Most of the reported methods are limited to the preparation of nortricyclenes bearing heteroatom substituents.^{6–10} In this paper, we describe a novel method for synthesizing aryl or benzyl substituted nortricyclenes from norbornadiene by using palladium complexes and zinc powder (eqn. 1).

The reactions were carried out on a 1-5 mmol scale with tetrahydrofuran as the solvent. A typical procedure is as follows. A mixture of Pd(PPh₃)₂Cl₂ (0.25 mmol), triphenylphosphine (0.50 mmol), zinc powder (80 mmol), norbornadiene (10 mmol), H₂O (10 mmol), aryl halide (5 mmol and THF (30 ml) was heated under nitrogen with stirring at 60 °C for 12-18 h. The THF solution was cooled, filtered and concentrated, and the residue purified by passing through a short column of silica gel using ethyl acetate-hexane as the eluent to give the product. The results are given in Table 1. All the products exhibit spectral data characteristic of the substituted cyclopropane ring including a sharp absorption at ca. 810 cm⁻¹ in the IR spectra, 6,11,12 absorptions at δ ca. 1.2 in the ¹H NMR spectra and absorptions at δ *ca.* 10 in the ¹³C NMR spectra. The ¹H and ¹³C chemical shifts for the cyclopropane group in nortricyclenes appear at higher field than is normal for a similar substitution pattern.¹³⁻¹⁵ The products were further identified by spectroscopic comparison with known similar compounds.6

The yields of nortricyclenes depend greatly on the concentration of norbornadiene. With the reactants present in the same molar ratios as in the procedure just described, the best isolated yield was obtained with a concentration of norbornadiene of *ca*. $0.3 \text{ mol } \text{dm}^{-3}$. Competitive polymerization of norbornadiene also occurs, to an extent which increases as its concentration increases, lowering the yield of nortricyclene.

The results in Table 1 show that many aryl halides react with norbornadiene under the present conditions to afford the corresponding substituted nortricyclenes in good yields. However, aryl halides with a nitro or hydroxy group do not yield the expected products. Esterification of *p*-iodophenol prior to reaction gives the corresponding nortricyclene in moderate yield (run 13). In general, aryl bromides afford lower yields. The addition of potassium iodide in the reaction of bromobenzene dramatically improves the yield (run 16). Presumably, halide exchange between the aryl bromide and iodide anion takes place to give the corresponding aryl iodide during the reaction.¹⁶⁻²⁰ Such exchange processes have been observed in the presence of nickel or palladium complexes. As expected, benzyl bromide also reacts with norbornadiene to afford the corresponding nortricyclene but in low yield. A large portion of the benzyl bromide is converted to toluene



(runs 18, 19). Other alkyl reagents that have been tested, including methyl α -chloroacetate and allyl acetate, do not react with norbornadiene to give nortricyclenes.

The yield of substituted nortricyclene is affected greatly by the solvent and the catalyst used. In toluene, acetonitrile or dimethylformamide (DMF), the yields of products were much lower than in THF. While the replacement of $Pd(PPh_3)_2Cl_2$ and PPh₃ by $Pd(PPh_3)_4$ (runs 1 and 4) gave the same yield of the expected nortricyclene within experimental error, the use of $PdCl_2$ or $Pd(OAc)_2$ in the absence of PPh₃ as catalyst affords essentially no desired product. Other metal complexes such as NiCl₂ or Ni(PPh₃)₂Cl₂ in the presence of zinc powder also do not catalyse reaction (1).

Although zinc powder serves as a reducing agent in the present reaction, its role is not yet clear. In the absence of zinc powder, the reaction of $Pd(PPh_3)_4$ with PhI, norbornadiene and water does not lead to the formation of the expected nortricyclene, and so zinc powder plays a key role. Recently, Larock and his coworkers²¹ investigated the reaction of norbornadiene with PhI in the presence of $Pd(OAc)_2$ and HCO_2K . Nortricyclene was not detected, but *exo*-2-phenyl-norborn-5-ene was isolated. In this reaction HCO_2K was the reducing agent and the hydrogen donor for the reaction. Their

Table 1ª Addition of organic halides to norbornadiene

Entry	Organic halides	Reaction time/h	Yield ^b (%)
1	PhI	12	89(72)
2 ^c	PhI	20	(40)
3d	PhI	12	65
4 <i>e</i>	PhI	20	86
5	<i>m</i> -MeOC ₆ H ₄ I	14	93
6	o-MeOC ₆ H ₄ I	14	70
7	p-MeOC ₆ H ₄ I	14	82(68)
8	p-MeC ₆ H ₄ I	14	82
9	1-C ₁₀ H ₇ I	14	88g
10	p-MeCOC ₆ H ₄	14	(87)
11	p-NO ₂ C ₆ H ₄ I	32	0
12	p-HOC ₆ H ₄ I	48	0
13	p-MeCO ₂ C ₆ H ₄ I	14	(48)
14	p-ClC ₆ H ₄ I	14	$(85)^{h}$
15	$2 - C_4 H_3 SI^i$	18	58(48)
16	PhBr	38	54 <i>i</i>
17	PhBr	40	32
18	PhCH ₂ Br	13	15^{k}
19	PhCH ₂ Br	12	35 <i>j</i> , k

^{*a*} All reactions were carried out following the procedure described in the text, unless otherwise noted. ^{*b*} GC yields. Isolated yields are in parentheses. ^{*c*} The concentration of norbornadiene was kept at 3.33 mol dm⁻³. ^{*d*} No extra PPh₃ was added. ^{*e*} Pd(PPh₃)₄ was the catalyst; no extra PPh₃ was added. ^{*f*} 1-Iodonaphthalene. ^{*g*} Yield was determined by ¹H NMR spectroscopy. ^{*h*} The chloro substituent was left untouched. ^{*i*} 2-Iodothiophene. ^{*j*} 2 equiv. of KI relative to PhBr was added; bromobenzene was recovered in 35% yield. ^{*k*} Toluene was the major product.

results and those in Table 1 strongly indicate that reducing agents are involved in determining the type of product formed.

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