Palladium(0)-Catalyzed Allylation of Highly Acidic and Nonnucleophilic Anilines. The Origin of Stereochemical Scrambling When Using Allylic Carbonates

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Acidic anilines such as diphenylamine, phenothiazine, and nitroanilines are efficiently allylated under palladium catalysis using allyl carbonates as allylating reagents. A stereochemical study of the reactions of ethyl *cis*-5-methyl-2-cyclohexenylcarbonate with 4-nitro- and 2,4-dinitroaniline was performed. Bidentate phosphines as stabilizing ligands gave clean retention of configuration whereas triphenylphosphine permitted cis−trans isomerization of the allylic carbonate, the allylation reactions occurring under Curtin−Hammet preequilibrium conditions.

Introduction

The palladium(0)-catalyzed allylation of nucleophiles (the Tsuji−Trost reaction) is a synthetic method highly accepted due to its broad applicability and facile experimental procedure.[1] The catalytic cycle requires the formation of the cationic η^3-allylpalladium(II) complex, an intermediate which can be attacked by nucleophiles at both termini of the allylic system. Depending on the nature of the nucleophile, two different stereochemical behaviors have been identified; thus, the first step is the formation of the cationic η^3-allylpalladium(II) intermediate, which occurs with inversion of configuration on the allyl system as a rule[2] not without exception.[3] This is exemplified in Figure 1 by the transformation of the stereochemical model ***cis*-1** into intermediate ***trans*-2** (stabilizing ligands have been omitted). Many common nucleophiles attack the cationic palladium intermediate with a new inversion of configuration (from ***trans*-2** to ***cis*-4**), thus affording the final product with overall retention of configuration.[1,4] On the other hand, nucleophiles such as organometallics of the type C-Metal (Metal = Mg, Al, Zr, Sn, B) bind to the palladium in a transmetalation step (***trans*-2** to ***trans*-3**) followed by intramolecular delivery or reductive elimination which takes place with retention of configuration (***trans*-3** into ***trans*-4**). This results in overall inversion of configuration.[1] Stereochemical models **1** have been used for nucleophiles C−Zn,[5a] C−Al,[5a] Si−Al,[5b] C−Sn,[3b,5c,d] C−Mg,[5e] Si−Si,[5f] C−B (under Ni(0) catalysis),[5g,h] carbon monoxide,[5c,i] and certain hydride donors.[5j]

Aliphatic amines[6a,b,7] frequently give both stereoisomers when reacting, as outlined in the stereochemical model of Figure 1, and the origin of trans final products when starting from a cis isomer has been attributed to three different factors:

(1) Equilibration of the isomeric starting materials ***cis*-1** and ***trans*-1** (top part of Figure 1). The leaving group X^- from ***cis*-1** attaches to Pd in the cationic intermediate ***trans*-2** to give neutral complex ***trans*-5**, which by reductive elimination completes the isomerization to ***trans*-1**. Of course, this process works in the other direction also (from ***trans*-1** to ***cis*-2**, ***cis*-5**, and ***cis*-1**). Isomerization of cyclic allylic acetates (**1**, X = OAc) has been proved.[2a,7−10] Since for amine nucleophiles

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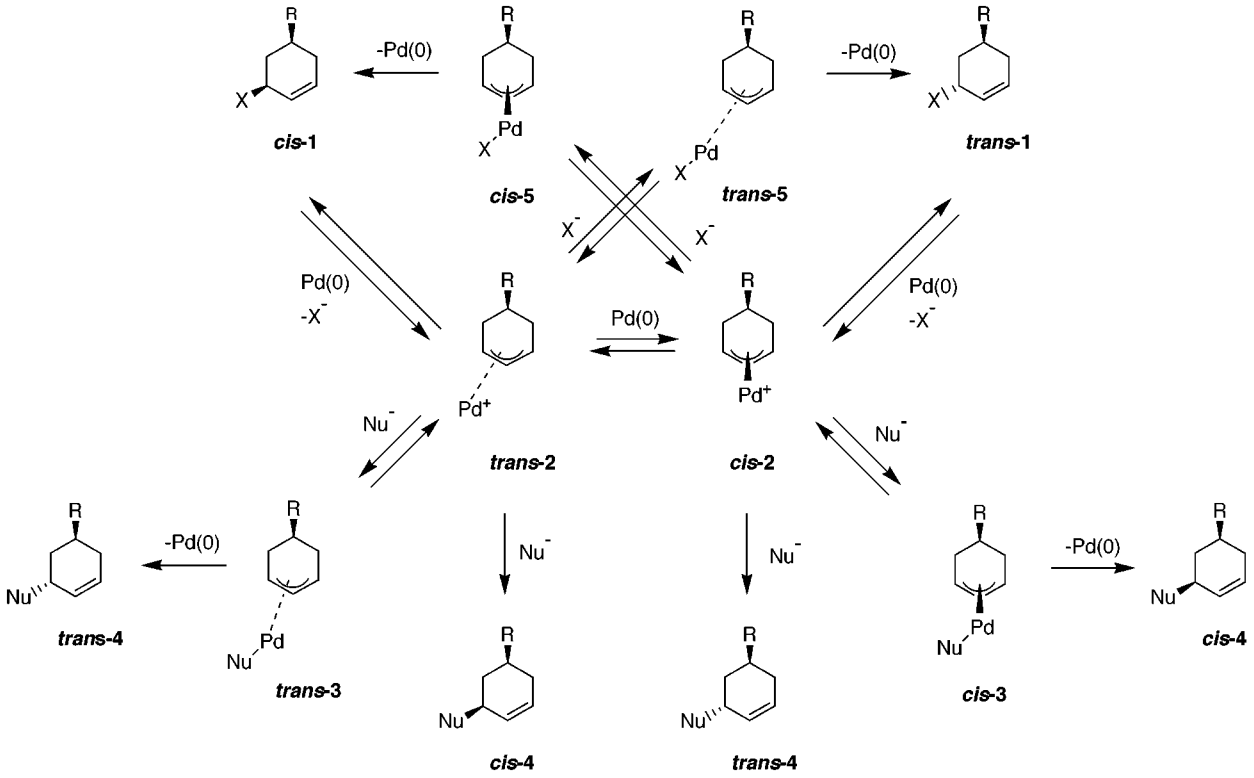

Figure 1. All stereochemical possibilities in the Pd-catalyzed allylation of nucleophiles.

sometimes overall inversion products are significant without acetates isomerization being observed,[6b] other mechanisms should be active in stereochemical scrambling.

(2) Actual retention of configuration in the second step as above-discussed (from ***cis*-1** to ***trans*-2**, ***trans*-3**, and ***trans*-4** and the same from the isomeric starting material).[6] It is reasonable to assume that heteroatom-based nucleophiles have more propensity to bind to the metal atom, therefore being more prone to a second step with retention of configuration.[6c]

(3) Cationic intermediate isomerization by nucleophilic attack of Pd, or rather PdL_2, to ***trans*-2** with inversion of configuration (S_N2 type mechanism) to afford ***cis*-2** and the other way around. Convincing evidence for the operation of this mechanism has been given by Bäckvall,[7a,b] and the cationic intermediate equilibration mechanism has been invoked by us[9] and others.[5g,11]

Other important factors to consider concerning the stereochemical outcome of the Pd-catalyzed allylation of nucleophiles are the nature (mono or bidentate) of the stabilizing phosphine, the leaving group ability, and the nucleophilic strength. A summary of the situation is as follows:

(1) Bidentate phosphines give much clear overall retention stereochemistry since they do not easily permit bonding of the leaving group or of the incoming nucleophile to the palladium atom. This militates against equilibration of starting materials and against retention of configuration in the second step.[7,9,11−13] On the other hand, the cationic intermediate equilibration is slow with bidentate phosphines.[7b] For monodentate phosphines a high phosphine:Pd ratio makes the same effects.[2a,9]

(2) Good leaving groups (e.g. trifluoroacetoxy with respect to acetoxy) cause all palladium to be present in the form of cationic complex, with no palladium remaining outside the allylic framework as PdL_n, and therefore rendering the S_N2 type mechanism less operative.[5g,7]

(3) Active nucleophiles reacting fast give less oportunity for equilibration of starting materials and/or cationic intermediates to occur.[2a,8]

The behavior of phenols in palladium(0)-catalyzed allylations has been throughly studied, including stereochemical experiments (bidentate phosphine) which showed the preference for an overall retention (double inversion) mechanism.[13] This is in contrast with the scarcity of data on the allylation of anilines.[14]

In an investigation aimed to define the scope of 2,4,6-triphenylpyridinium salts as substrates in the Tsuji−Trost reaction (2,4,6-triphenylpyridine as leaving group), we included 2,6-dimethylaniline as one of the studied nucleophiles[15] and we found products of allylation at the *para* carbon atom, an analysis of them driving us to hypothesize a pathway including attachment of the

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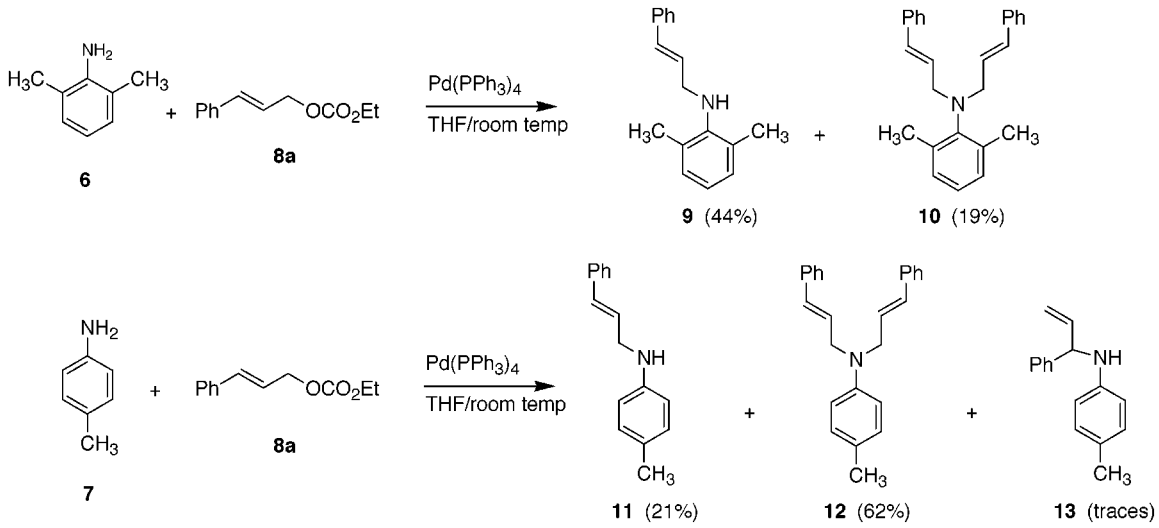
Scheme 1. Pd-Catalyzed Allylation of Simple Anilines



aniline to the palladium atom followed by intramolecular delivery or reductive elimination with retention of configuration (overall inversion), as proposed previously for aliphatic amines.[6a] At this point we decided to undertake a study of the Pd-catalyzed allylation of nonnucleophilic anilines (i.e. 4-nitroaniline and the like). These anilines are more acidic than alcohols in DMSO and the order of acidity is probably maintained in tetrahydrofuran (THF),[16] which should permit one to work with allylic carbonates as substrates (leaving group X = OCOOEt) that in situ produce CO_2 and ethoxide anion[17] basic enough to take a proton from the aniline. Cyclic allylic carbonates have been used as stereochemical probes,[5h,7,11b,13,18,19] although one case of cis−trans equilibration under Pd-catalysis has been reported.[20]

Results and Discussion

First we studied the reactions of simple anilines such as 2,6-dimethylaniline, **6**, and *p*-toluidine, **7**, with cinnamyl ethyl carbonate, **8a** (Scheme 1). Both anilines were very active, and in the presence of 5% molar tetrakis(triphenylphosphine)palladium(0) at room temperature, they gave products of reaction at the nitrogen atom. When equimolar amounts of anilines and **8a** were introduced, dialkylation products were significant or even predominant.

Next we moved to more acidic amines (Scheme 2).[21] Diphenylamine, **14**, reacted at room temperature with allyl carbonates **8a,b** to afford *N*-allylation products **19a,b** in high yields. Phenothiazine, **15**, behaved the same. 2-Nitroaniline, **16**, gave only a moderate yield of *N*-cinnamyl-2-nitroaniline, **21**, under similar experimental conditions, but its para isomer, **17**, free of steric constraints, gave mostly the diallylated **23** when a 4-fold molar excess of carbonate **8a** was introduced. The sterically more demanding 2-cyclohexenyl ethyl carbonate, **8c**, was also an efficient allylation reagent for **17** and for the more acidic but also more crowded 2,4-dinitroaniline, **18**, although at reflux temperature.

Then we performed a stereochemical study of the reactions of acidic anilines **17** and **18** with the stereochemically defined ethyl *cis*-5-methyl-2-cyclohexenyl carbonate,[9] ***cis*-8d** (Scheme 3). Table 1 summarizes the results obtained with 4-nitroaniline. The most evident result is that the optimal conditions for overall retention of configuration require the use of a bidentate phosphine such as bis(diphenylphosphino)ethane (dppe). Thus, experiment 14 gives the highest ***cis*-26:*trans*-26** ratio and, when performed at a preparative scale, produces ***cis*-26** in 95% yield. The bidentate phosphine gives the cationic intermediate ***trans*-28** (Scheme 3), where both phosphorus atoms pertain to the same ligand and it reacts with the conjugate base of **17** to afford ***cis*-26** in a clean overall retention reaction. However, when using $Pd(PPh_3)_4$, stereochemical scrambling was observed (Table 1). Independent blank experiments in the absence of nucleophile indicated:

(1) Equilibration of allylic carbonate, ***cis*-8d**, with its isomer ***trans*-8d** (^{1}H NMR and GLC monitoring) takes place at room temperature in the presence of $Pd(PPh_3)_4$ in THF, the equilibrium ratio ***cis*-8d:*trans*-8d** (41:59) being reached between 35 and 70 min and remaining the same until both carbonates disappear, probably by elimination to afford cyclohexadienes. Indirectly, we were also informed that loss of carbonic anhydride is slow enough for isomerization to be observed.

(2) Equilibration of carbonates **8d** was not produced in the presence of $Pd(dba)_2$:dppe at room temperature in THF (Scheme 3). The starting ratio ***cis*-8d:*trans*-8d** (97:3) remained unchanged at 6 h and was converted to 95:5 at 24 h.

(3) Equilibration of carbonates **8d** was observed in the presence of $Pd(dba)_2$:dppe in refluxing THF. The ratio ***cis*-8d:*trans*-8d** (initially 97:3) was 96:4 at 5 min and 74:26 at 35 min.

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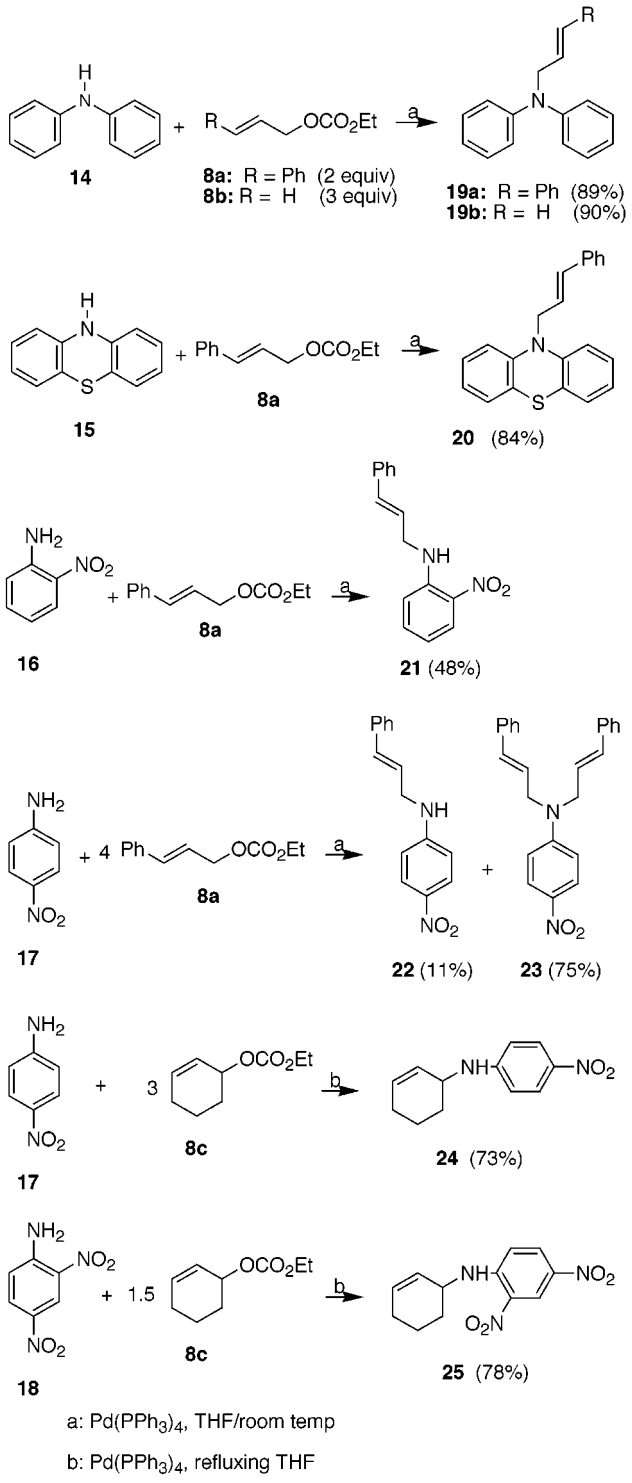
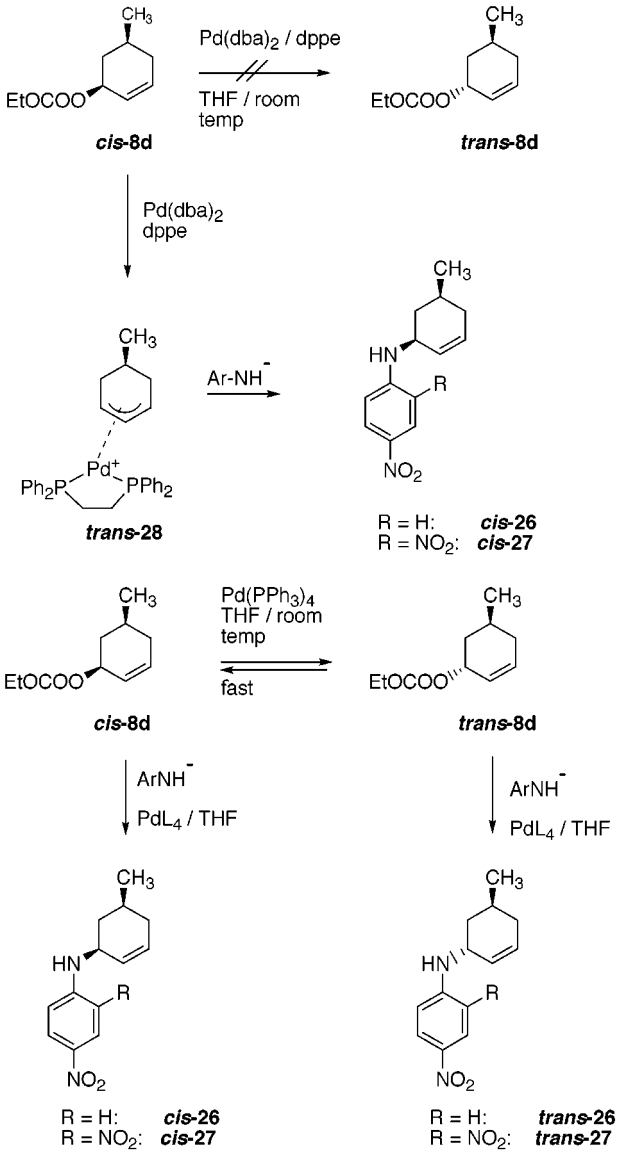
(21) pK_a values in DMSO of amines of Scheme 2 according to ref 16: diphenylamine, **14**, 24.95; phenothioazine, **15**, 22.7; 4-nitroaniline, **17**, 20.9; 2,4-dinitroaniline, **18**, 15.9 as compared with methanol (29.0) and with aniline (30.6).

Scheme 2. Pd-Catalyzed Allylation of Acidic Anilines



Isomerization of carbonates is represented in the top part of Scheme 4 (pathway ***cis*-8d** to ***trans*-29**, ***trans*-30**, and ***trans*-8d**) and is favored by the elimination of a phosphine ligand from the metal, which can be replaced by the leaving group. Nucleophilic attack with inversion of configuration on each of the equilibrated cationic intermediates ***trans*-29** and ***cis*-29** affords the mixture of isomeric anilinocyclohexenes **26**. When using triphenylphosphine, isomerization of carbonates is faster than the formation of final products **26**. Thus, an experiment was performed consisting of the reaction of ***cis*-8d** with 4-nitroaniline, **17**, in the presence of $Pd(PPh_3)_4$ in THF

Scheme 3. Stereochemical Results of the Pd-Catalyzed Reactions of *cis*-8d with Nitroanilines 17 and 18



at room temperature; at 35 min the ratio ***cis*-8d:*trans*-8d** was already 69:31 and the ratio ***cis*-26:*trans*-26** was 63:37. At 3 h 50 min the ratio of carbonates had reached the equilibrium (42:58) and the ratio of final products was 68:32. These ratios remained unchanged after 3 days. Therefore, the system is under Curtin−Hammett preequilibrium conditions and the ratio of final products is independent of the ratio of starting materials and is only dependent on the difference in Gibbs energies $\Delta\Delta G^{\ddagger}$ between the transition states leading to both final products.

Having established the role of carbonate equilibration in the stereochemical outcome, we paid attention to the contribution of the cationic intermediate isomerization mechanism, equilibrating ***trans*-29** with ***cis*-29**. From Table 1 (entries 1−5) it is evident that the ***cis*-26:*trans*-26** ratio is somehow dependent on the ratio Pd:P. Concentration of PdL_2 depends on the position of equilibria in eqs 1 and 2 and it is diminished by increasing the overall quantity of L. Indeed, a low concentration of PdL_2 will slow also the formation of cationic intermediate ***trans*-29**, but simple kinetic considerations lead to the

Table 1. Stereochemical Results of the Pd(0)-Catalyzed Reactions of 4-Nitroaniline, 17, with Carbonate *cis*-8d[a]

entry	**17**:***cis*-8d**	Pd source (%)	Pd:P	***cis*-26**:***trans*-26**[b]
1	1:4	$Pd(PPh_3)_4$ (5%)	1:4	62:31 (67:33)
2	1:4	$Pd(PPh_3)_4$ (5%)	1:8[c]	65:30 (68:32)
3	1:4	$Pd(PPh_3)_4$ (5%)	1:12[c]	69:28 (71:29)
4	1:4	$Pd(PPh_3)_4$ (5%)	1:20[c]	70:24 (74:26)
5	1:4	$Pd(PPh_3)_4$ (5%)	1:28[c]	77:20 (79:21)
6	1:4	$Pd_2(dba)_3$ (5%)	1:1[c]	23:3 (88:12)
7	1:4	$Pd_2(dba)_3$ (5%)	1:2[c]	47:6 (87:13)
8	1:4	$Pd_2(dba)_3$ (5%)	1:4[c]	64:27 (70:30)
9	1:4	$Pd_2(dba)_3$ (5%)	1:2[d]	57:18 (76:24)
10	1:4	$Pd_2(dba)_3$ (5%)	1:4[d]	63:30 (68:32)
11	1:4	$Pd_2(dba)_3$ (5%)	1:2[e]	21:2 (91:9)
12	1:4	$Pd_2(dba)_3$ (5%)	1:4[e]	45:3 (94:6)
13	1:1	$Pd_2(dba)_3$ (5%)	1:2[e]	63:3 (95:5)
14	1:2	$Pd_2(dba)_3$ (5%)	1:2[e]	88:3 (97:3)

[a] Overnight in refluxing THF. Amine concentration ca. 0.4 M. [b] GLC areas, aniline **17** accounts for the difference to 100%; in parentheses ratios are corrected to sum 100. [c] Excess P added as PPh_3. [d] Excess P added as tri-*o*-furylphosphine. [e] Excess P added as 1,2-bis(diphenylphosphino)ethane (1 mol = 2 mol of P).

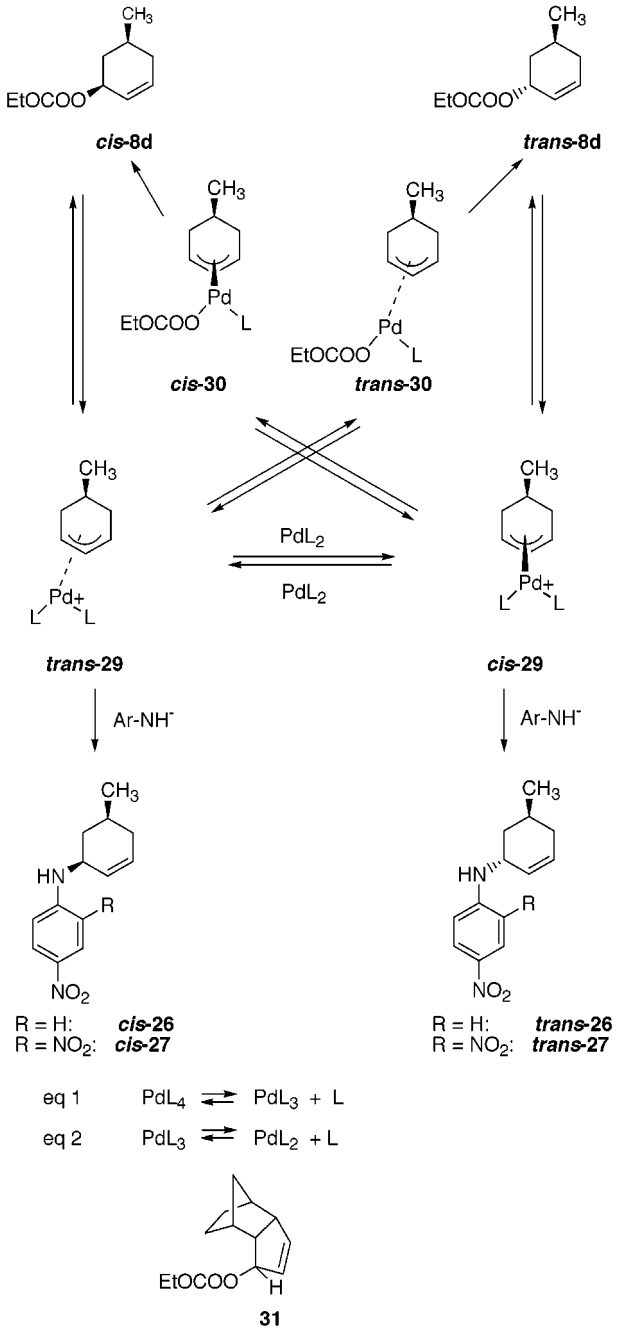
conclusion that equilibration of cationic intermediates should be more sensitive to $[PdL_2]$ since PdL_2 acts consecutively twice for the equilibrium of intermediates to be reached.[9] At low Pd/P ratios the direct displacement equilibration is diminished or supressed and experiment 5 shows a result which is probably due only to the Curtin−Hammett preequilibrium conditions of the system as above-discussed.

The results with the more acidic 2,4-dinitroaniline, **18**, are summarized in Table 2. As before, bidentate phosphines such as 1,1′-bis(diphenylphosphino)ferrocene (dppf) and dppe strongly favor the overall retention (entries 8−10). However, use of triphenylphosphine produces again stereochemical scrambling in this case in slight preference for the ***trans*-27** isomer, which is always the major product, independently of the Pd source. This is unusual since it implies that one or another of the isomeric final products can be obtained exclusively or predominantly from the same starting materials under different catalytic conditions. As for **17**, increasing the ratio triphenylphosphine:Pd slightly increases the percentage of isomer ***cis*-27**. However, even for a P:Pd value of 28 (entry 4) the major isomer is ***trans*-27** (60%). By working with P:Pd values as low as 2 (entry 6), the ratio of isomers is maintained in the same range of values as in the previous entries.

Again, with respect to carbonate isomerization, the system is under Curtin−Hammett preequilibrium conditions, as evidenced by the analysis of the reaction between ***cis*-8d** and 2,4-dinitroaniline, **18**, in THF at room temperature in the presence of $Pd(PPh_3)_4$; at 3 h 30 min the ratio ***cis*-8d**:***trans*-8d** was already 46:54 and the ratio ***cis*-27**:***trans*-27** was 23:73. The final ratios 42:58 (equilibrium of carbonates) and 24:76 for ***cis*-27**:***trans*-27** were reached after a bit longer and were mantained at 3 days of reaction. An additional experiment showed that ***cis*-27** did not isomerize to ***trans*-27** in the presence of $Pd(PPh_3)_4$ in THF at 80 °C.

Since conjugate bases of acidic anilines are potentially good ligands for palladium, the possibility remains that isomers ***cis*-26** and ***cis*-27** come from cation ***cis*-29** through aniline bonding to Pd followed by reductive elimination with retention. Analogously ***trans*-26** and ***trans*-27** could be formed from ***trans*-29**. This possibility was difficult to prove or disprove at this stage. Therefore, we prepared carbonate **31**; its related acetate has been reported to react only by the overall inversion pathway (inversion + retention) since an inversion in the second step is hampered by steric constraints.[22] Carbonate **31** did not react with 2,4-dinitroaniline, **18**, under a vast array of forcing experimental conditions including mono- and bidentate phosphines and higher temperatures. This is indirect evidence that the overall retention pathway is very predominant if not exclusive for the studied acidic anilines.

Scheme 4. Mechanistic Details of the Pd-Catalyzed Reactions of *cis*-8d with Nitroanilines 17 and 18



The mechanistic conclusions rely upon the correct assignment of configuration to pairs of isomers **26** and **27**. This was done by standard NMR correlations to assign all signals in each isomer and NOE measurements. The results are summarized in Schemes 5 and 6 and are in agreement with the reported conformational

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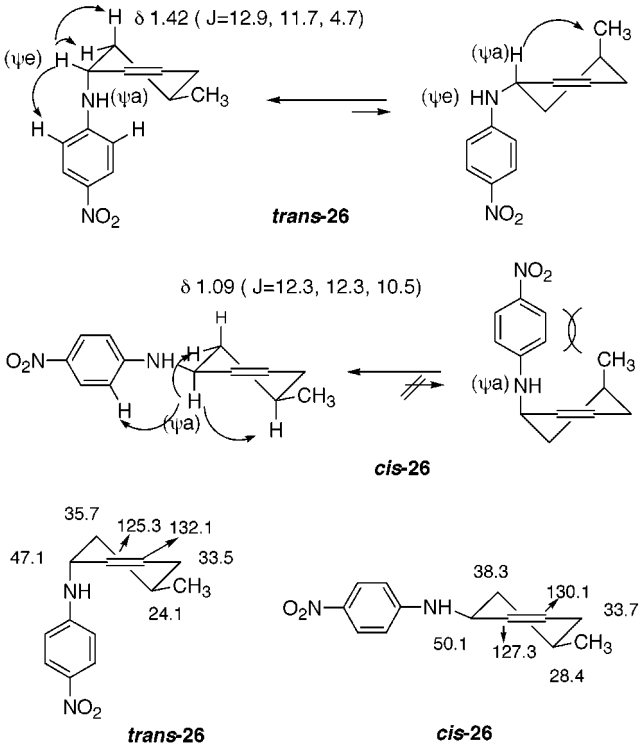
Table 2. Stereochemical Results of the Pd(0)-Catalyzed Reactions of 2,4-Dinitroaniline, 18, with Carbonate *cis*-8d[a]

entry	Pd source (%)	Pd:P	*cis*-27:*trans*−27[b]
1	$Pd(PPh_3)_4$ (5%)	1:4	28:72
2	$Pd(PPh_3)_4$ (5%)	1:12[c]	30:70
3	$Pd(PPh_3)_4$ (5%)	1:20[c]	33:67
4	$Pd(PPh_3)_4$ (5%)	1:28[c]	40:60
5	$Pd_2(dba)_3$ (5%)	1:4[c]	31:69
6	$Pd_2(dba)_3$ (5%)	1:2[c]	32:68
7	$Pd_2(dba)_3$ (5%)	1:1[c]	no reaction
8	$Pd_2(dba)_3$ (5%)	1:3[d]	96:4
9	$Pd_2(dba)_3$ (5%)	1:1[d]	95:5
10	$Pd_2(dba)_3$ (5%)	1:3[e]	96:4

[a] Overnight in refluxing THF, ratio **18**:*cis*-**8d** = 1:2 in all cases. Amine concentration ca. 0.4 M. [b] GLC areas, reactions finished but for entry 7. [c] Excess P added as PPh_3. [d] Excess P added as 1,1′-bis(diphenylphosphino)ferrocene (1 mol = 2 mol of P). [e] Excess P added as 1,2-bis(diphenylphosphino)ethane (1 mol = 2 mol of P).

Scheme 5. Relevant NMR Data and Positive NOE for *cis*-26 and *trans*-26

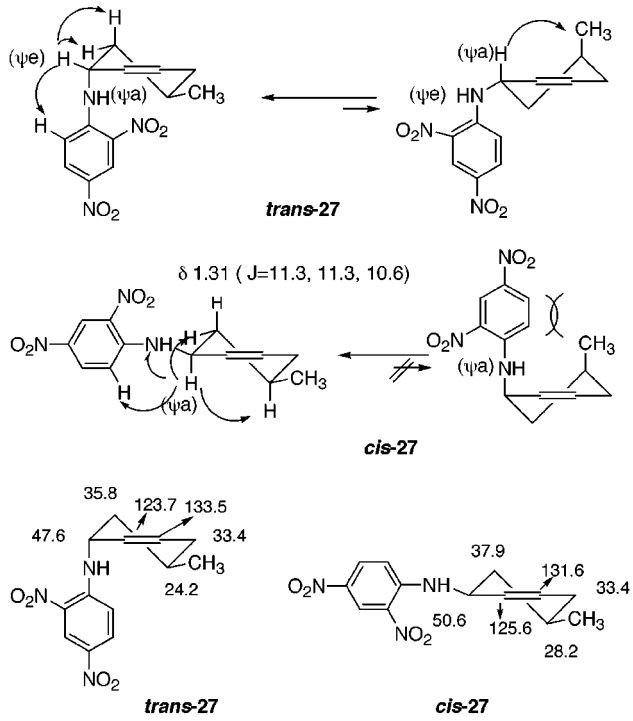


behavior of substituted cyclohexenes,[6b,8,9,23,24] and with previous stereochemical assignments to pairs of *cis*- and *trans*-3,5-disubstituted cyclohexenes.[2a,4a,5c,h,7b,9,11a]

Experimental Section

All reactions under Pd catalysis were performed under inert atmosphere with anhydrous solvents. Syringes or cannulae were used for transfer of solutions. As a general procedure, a solution of the catalyst and the allylating agent in THF is added onto a solution of the nucleophile in the same solvent. For elemental analysis purposes some oily anilines were converted into crystalline 1,5-naphthalenedisulfonates (stoichiometry 2:1) by mixing with naphthalene-1,5-disulfonic acid in methanol and collecting the precipitate.

Scheme 6. Relevant NMR Data and Positive NOE for *cis*-27 and *trans*-27



***N*-Cinnamyl-2,6-dimethylaniline, 9, and *N*,*N*-Dicinnamyl-2,6-dimethylaniline, 10. General Method.** A solution of tetrakis(triphenylphosphine)palladium (447 mg, 0.413 mmol), cinnamyl ethyl carbonate, **8a**, (1.702 g, 8.25 mmol), and 2,6-dimethylaniline (1.000 g, 8.25 mmol) in anhydrous THF (50 mL) was stirred for 5 h at room temperature. The solution was filtered and the filtrate was evaporated to give a residue which was chromatographed through silica gel with mixtures of hexanes−dichloromethane of increasing polarity. The first product eluted was aniline **10** (543 mg, 19%): IR (film) 1597, 1473, 965, 769, 741, 693 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 2.37 (s, 6H), 3.81 (d, J = 6.6 Hz, 4H), 6.23 (dt, J = 15.9 and 6.6 Hz, 2H), 6.46 (d, J = 15.9 Hz, 2H), 6.92−7.06 (m, 3H), 7.15−7.39 (m, 10H); ^{13}C NMR (62.5 Hz, $CDCl_3$) δ 19.7, 55.2, 125.1, 126.2, 127.2, 128.5, 128.6, 128.8, 131.3, 137.2, 137.3, 148.3; naphthalene-1,5-disulfonate: mp 181−183 °C (methanol). Anal. Calcd for $C_{62}H_{62}N_2S_2O_6 \cdot H_2O$: C, 73.49; H, 6.37; N, 2.76; S, 6.33. Found: C, 73.11 and 72.96; H, 6.45 and 6.38; N, 2.79 and 2.78; S, 6.05 and 6.09. The second product eluted was aniline **9** (871 mg, 44%): IR (film) 3373, 1595, 1474, 966, 765, 742, 693 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 2.31 (s, 6H), 2.90 (br s, 1H), 3.74 (dd, J = 6.2 and 1.1 Hz, 2H), 6.35 (dt, J = 15.7 and 6.2 Hz, 1H), 6.61 (d, J = 15.7 Hz, 1H), 6.84 (t, J = 7.3 Hz, 1H), 7.01 (d, J = 7.3 Hz, 2H), 7.18−7.44 (m, 5H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 18.5, 50.8, 122.1, 126.3, 127.4, 128.1, 128.5, 128.8, 129.6, 131.2, 137.0, 145.7; naphthalene-1,5-disulfonate: mp 220−221 °C (methanol). Anal. Calcd for $C_{44}H_{46}N_2S_2O_6$: C, 69.27; H, 6.08; N, 3.67; S, 8.40. Found: C, 69.28 and 69.34; H, 5.76 and 5.78; N, 3.56 and 3.60; S, 8.14 and 7.99. 2,6-Dimethylaniline, **6**, (303 mg, 30%) was finally eluted.

***N*-Cinnamyl-4-methylaniline, 11, and *N*,*N*-Dicinnamyl-4-methylaniline, 12.** *N*-Cinnamyl-4-methylaniline, **11**, eluted second: oil, IR (film) 3409, 1617, 1520, 967, 808, 743, 692 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 2.21 (s, 3H), 3.51 (br s, 1H), 3.83 (dd, J = 5.8 and 1.4 Hz, 2H), 6.26 (dt, J = 16.0 and 5.8 Hz, 1H), 6.50−6.62 (m, 3H), 6.97 (d, J = 10.2 Hz, 2H), 7.05−7.35 (m, 5H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 20.3, 46.4, 113.2, 126.2, 126.6, 127.2, 127.3, 128.4, 129.6, 131.2, 136.8, 145.7. Compound **11** was previously described[25] and spectroscopic data are coincident. *N*,*N*-Dicinnamyl-4-methylaniline, **12**, eluted first: mp 79 °C (methanol); IR (KBr) 1619, 1522, 1493, 964, 801, 735, 695 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ

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2.24 (s, 3H), 4.06 (dd, J = 5.3 and 1.4 Hz, 4H), 6.24 (dt, J = 16.0 and 5.3 Hz, 2H), 6.51 (d, J = 16.0 Hz, 2H), 6.73 (d, J = 8.0 Hz, 2H), 7.05 (d, J = 8.0 Hz, 2H), 7.11−7.35 (m, 10H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 20.2, 52.4, 113.0, 125.8, 126.2, 126.3, 127.3, 128.5, 129.7, 131.2, 136.9, 146.8. Anal. Calcd for $C_{25}H_{25}N$: C, 88.45; H, 7.42; N, 4.13. Found: C, 88.11 and 88.27; H, 7.48 and 7.52; N, 4.15 and 4.15.

***N*-Cinnamyldiphenylamine, 19a.** This compound is an oil: IR (film) 1678, 1590, 1495, 1365, 1246, 1221, 966, 748, 694 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$) δ 4.48 (dd, J = 5.1 and 1.8 Hz, 2H), 6.30 (dt, J = 16.1 and 5.1 Hz, 1H), 6.56 (d, J = 16.1 Hz, 1H), 6.88−7.40 (m, 15H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 54.3, 120.8, 121.3, 126.1, 126.3, 127.3, 128.4, 129.2, 131.3, 136.9, 147.8. Anal. Calcd for $C_{21}H_{19}N$: C, 88.38; H, 6.71; N, 4.91. Found: C, 88.15 and 87.87; H, 6.52 and 6.63; N, 4.73 and 4.73.

***N*-Allyldiphenylamine, 19b.** This compound is an oil: IR (film) 1591, 1495, 1365, 1250, 1224, 920, 749, 695 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$) δ 4.36 (d, J = 4.7 Hz, 2H), 5.16 (d, J = 10.2 Hz, 1H), 5.26 (d, J = 17.2 Hz, 1H), 5.93 (ddt, J = 17.2, 10.2, and 4.7 Hz, 1H), 6.89−6.98 (m, 4H), 7.20−7.30 (m, 6H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 54.7, 116.4, 120.7, 121.2, 129.2, 134.2, 147.8. Anal. Calcd for $C_{15}H_{15}N$: C, 86.08; H, 7.22; N, 6.69. Found: C, 85.88 and 85.77; H, 6.98 and 6.90; N, 6.62 and 6.86.

***N*-Cinnamylphenothiazine, 20.** This compound is an oil: IR (film) 1676, 1572, 1594, 1464, 1446, 1364, 1254, 1218, 968, 747, 694 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$) δ 4.64 (d, J = 4.4, 2H), 6.36 (dt, J = 16.1 and 4.4 Hz, 1H), 6.58 (d, J = 16.1 Hz, 1H), 6.82−6.93 (m, 4H), 7.00−7.11 (m, 4H), 7.19−7.39 (m, 5H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 50.9, 115.3, 122.4, 122.9, 124.8, 126.3, 126.8, 127.3, 127.7, 128.6, 132.0, 136.4, 144.4; MS (m/z) 315 (M^+, 8), 199 (16), 198 (100).

***N*-Cinnamyl-2-nitroaniline, 21.** This compound presents the following data: mp 70−71 °C (dichloromethane−hexanes); IR (KBr) 3394, 1618, 1568, 1510, 1359, 1315, 1259, 971, 743, 689 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$) δ 4.12 (d, J = 5.5 Hz, 2H), 6.27 (dt, J = 15.7 and 5.5 Hz, 1H), 6.61 (d, J = 15.7 Hz, 1H), 6.65 (t, J = 7.8 Hz, 1H), 6.87 (d, J = 8.4 Hz, 1H), 7.19−7.46 (m, 6H), 8.18 (d, J = 8.8 Hz, 1H), 8.24 (s, 1H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 44.8, 114.0, 115.5, 124.6, 126.3, 126.7, 127.8, 128.5, 132.2, 136.1, 145.1. Anal. Calcd for $C_{15}H_{14}N_2O_2$: C, 70.85; H, 5.55; N, 11.02. Found: C, 70.84 and 70.75; H, 5.72 and 5.69; N, 10.98 and 11.00.

***N*-Cinnamyl-4-nitroaniline, 22, and *N,N*-Dicinnamyl-4-nitroaniline, 23.** Compound **22** presented the following data: mp 142−144 °C (dichloromethane−hexanes); IR (KBr) 3357, 1601, 1538, 1325, 1278, 1181, 1108, 972, 829, 784 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$) δ 4.03 (dd, J = 5.6 and 4.2 Hz, 2H), 4.75 (br s, 1H), 6.25 (dt, J = 16.1 and 5.6 Hz, 1H), 6.55−6.66 (m, 3H), 7.20−7.43 (m, 5H), 8.09 (d, J = 9.1 Hz, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 45.4, 111.3, 124.6, 127.9, 128.6, 132.7, 136.2, 138.2, 153.1.

Compound **23** presented the following data: mp 157−158 °C (dichloromethane−hexanes); IR (KBr) 1591, 1512, 1488, 1360, 1297, 1109, 972, 826, 801 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$) δ 4.25 (d, J = 5.1 Hz, 4H), 6.23 (dt, J = 16.0 and 5.1 Hz, 2H), 6.52 (d, J = 16.1 Hz, 2H), 6.75 (d, J = 9,5 Hz, 2H), 7.20−7.43 (m, 10H), 8.13 (d, J = 9.5 Hz, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 52.4, 110.9, 123.3, 126.2, 126.4, 127.9, 128.6, 132.2, 136.2, 137.4, 153.2. Anal. Calcd for $C_{24}H_{22}N_2O_2$: C, 77.81; H, 5.99; N, 7.56. Found: C, 77.55 and 77.53; H, 5.82 and 5.71; N, 7.55 and 7.42.

3-(4-Nitrophenylamino)cyclohexene, 24. Aniline **24** presented the following data: mp 100−101 °C; IR (KBr) 3402, 3027, 1605, 1526, 1308, 828, 747, 731 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.52−2.12 (m, 6H), 3.98−4.14 (m, 1H), 4.50 (br d, J = 6.7 Hz, 1H), 5.68 (m, 1H), 5.92 (m, 1H), 6.51 (d, J = 9.3 Hz, 2H), 8.05 (d, J = 9.3 Hz, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 19.3, 24.9, 28.5, 47.7, 111.3, 126.5, 126.6, 131.7, 137.8, 152.3. Anal. Calcd for $C_{12}H_{14}N_2O_2$: C, 66.04; H, 6.46; N, 12.84. Found: C, 66.08 and 66.08; H, 6.23 and 6.20; N, 12.66 and 12.70.

3-(2,4-Dinitrophenylamino)cyclohexene, 25. Aniline **25** presented the following data: mp 108 °C; IR (KBr) 3368, 1615, 1587, 1520, 1334, 1281 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.61−1.87 (m, 3H), 1.94−2.24 (m, 3H), 4.26 (br s, 1H), 5.70 (m, 1H), 6.02 (m, 1H), 6.96 (d, J = 9.5 Hz, 1H), 8.23 (dd, J = 9.5 and 2.9 Hz, 1H), 8.55 (d, J = 7.3 Hz, 1H), 9.11 (d, J = 2.9 Hz, 1H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 19.3, 24.7, 28.5, 48.3, 114.1, 124.6, 125.0, 130.2, 130.5, 133.0, 135.8, 147.4; MS (m/z) 263 (M^+, 3), 81 (100), 79 (32), 41 (23). Anal. Calcd for $C_{12}H_{13}N_3O_4$: C, 54.75; H, 4.98; N, 15.96. Found: C, 54.83 and 54.77; H, 4.95 and 4.83; N, 15.71 and 15.63.

***cis*- And *trans*-5-Methyl-3-(4-nitrophenylamino)cyclohexene, *cis*-26 and *trans*-26.** Isomer ***cis*-26** was eluted second when obtained as a mixture of isomers and presented the following data: mp 88−89 °C; IR (KBr) 3385, 1602, 1539, 1501, 1308, 824, 747, 690 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.98 (d, J = 6.5 Hz, 3H), 1.09 (ddd, J = 12.3, 12.3, and 10.5 Hz, 1H), 1.58−1.71 (m, 1H), 1.72−1.90 (m, 1H), 2.05−2.19 (m, 2H), 4.10−4.21 (m, 1H), 4.51 (d, J = 7.7 Hz, 1H), 5.55−5.62 (m, 1H), 5.78−5.86 (m, 1H), 6.51 (d, J = 9.3 Hz, 2H), 8.03 (d, J = 9.3 Hz, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 21.9, 28.4, 33.7, 38.3, 50.1, 111.3, 126.5, 127.3, 130.3, 137.7, 152.5. Anal. Calcd for $C_{13}H_{16}N_2O_2$: C, 67.22; H, 6.94; N, 12.06. Found: C, 67.19 and 67.14; H, 7.01 and 7.02; N, 11.95 and 12.02. Isomer ***trans*-26** was eluted first and presented the following data: mp 104−105 °C; IR (KBr) 3398, 1602, 1523, 1501, 1465, 1306, 827, 724, 691 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.98 (d, J = 6.5 Hz, 3H), 1.42 (ddd, J = 12.9, 11.7, and 4.7 Hz, 1H), 1.60−1.90 (m, 2H), 2.14 (m, 1H), 4.01−4.10 (m, 1H), 4.61 (d, J = 6.4 Hz, 1H), 5.68−5.77 (m, 1H), 5.90−5.98 (m, 1H), 6.50 (d, J = 9.4 Hz, 2H), 8.04 (d, J = 9.4 Hz, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 21.5, 24.1, 33.5, 35.7, 47.1, 111.1, 125.2, 126.5, 132.1, 137.7, 152.0.Anal. Calcd for $C_{13}H_{16}N_2O_2$: C, 67.22; H, 6.94; N, 12.06. Found: 67.34 and 67.42; H, 7.00 and 7.09; N, 11.97 and 12.01.

***cis*- And *trans*-5-Methyl-3-(2,4-Dinitrophenylamino)cyclohexene, *cis*-27 and *trans*-27.** Isomer ***cis*-27** was eluted first when obtained as a mixture of isomers and presented the following data: mp 86−87 °C; IR (KBr) 3342, 1617, 1520, 1331, 719 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.03 (d, J = 6.6 Hz, 3H), 1.31 (ddd, J = 11.3, 11.3, and 10.6 Hz, 1H), 1.68−1.79 (m, 1H), 1.82−1.96 (m, 1H), 2.13−2.23 (m, 2H), 4.33−4.43 (m, 1H), 5.58−5.64 (m, 1H), 5.91−5.97 (m, 1H), 6.97 (d, J = 9.7 Hz, 1H), 8.22 (dd, J = 9.7 and 2.7 Hz, 1H), 8.53 (br d, J = 7.0 Hz, 1H), 9.11 (d, J = 2.7 Hz, 1H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 21.8, 28.2, 33.4, 37.9, 50.6, 114.2, 124.6, 125.6, 130.2, 130.3, 131.7, 135.8, 147.7; MS (m/z) 277 (M^+, 6), 95 (100), 67 (44), 55 (15) 41 (24). Anal. Calcd for $C_{13}H_{15}N_3O_4$: C, 56.31; H, 5.45; N, 15.15. Found: C, 56.52 and 56.50; H, 5.43 and 5.53; N, 14.85 and 14.93. Isomer ***trans*-27** was eluted second and presented the following data: mp 168−171 °C; IR (KBr) 3367, 1584, 1521, 1422, 1328 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.99 (d, J = 6.5 Hz, 3H), 1.52−1.62 (m, 1H), 1.65−1.75 (m, 1H), 1.77−1.90 (m, 2H), 2.24 (m, 1H), 4.24−4.31 (m, 1H), 5.74−5.81 (m, 1H), 6.03−6.09 (m, 1H), 6.97 (d, J = 9.7 Hz, 1H), 8.24 (dd, J = 9.7 and 2.7 Hz, 1H), 8.54 (d, J = 6.8 Hz, 1H), 9.12 (d, J = 2.7 Hz, 1H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 21.4, 24.2, 33.4, 35.8, 47.6, 114.0, 123.7, 124.6, 130.3, 130.6, 133.5, 135.8, 147.2; MS (m/z) 277 (M^+, 5), 95 (100), 67 (41), 55 (23), 41 (21). Anal. Calcd for $C_{13}H_{15}N_3O_4$: C, 56.31; H, 5.45; N, 15.15. Found: 56.51 and 56.55; H, 5.51 and 5.53; N, 14.88 and 14.86.

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Supporting Information Available: IR, ^{1}H NMR, and ^{13}C NMR spectra of all allylated anilines (38 pages). Ordering information is given on any current masthead page. This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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