

## Palladium(II)-Catalyzed Michael-Type Hydroarylation of Nitroalkenes Using Aryltins and Sodium Tetraarylborates

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A variety of aryltin compounds and sodium tetraarylborates can be employed for Michael-type hydroarylation reactions of nitroalkenes to afford  $\beta$ -arylnitroalkanes in moderate to good yields in the presence of either LiCl, MgCl<sub>2</sub>, or CaCl<sub>2</sub> and a catalytic amount of palladium(II) salt (0.05 molar amount) in acetic acid. Results show that 50–70% of aryl groups out of all in these aryl compounds can be transferred to the products in this hydroarylation. The addition of a catalytic amount (0.05–0.10 molar amount) of a Lewis acid chloride, BiCl<sub>3</sub> or SbCl<sub>3</sub>, much improves the product yield in some cases.

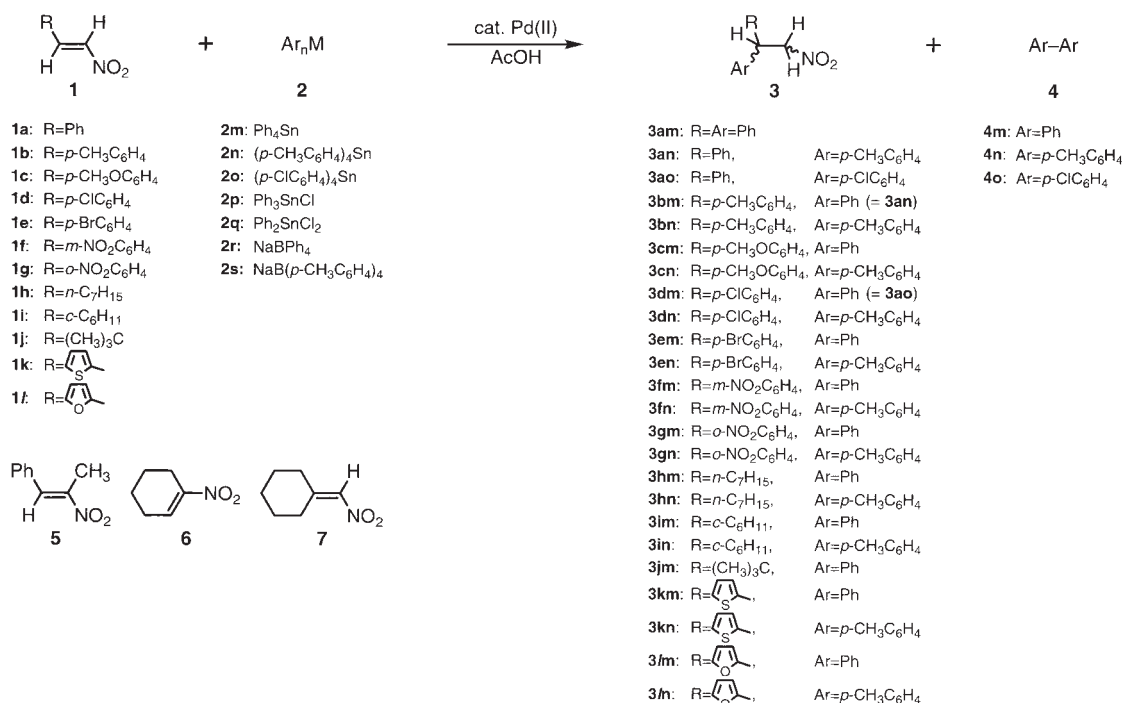
A variety of organoheteroatom compounds such as organoborons,<sup>1</sup> organotin,<sup>2</sup> and organoantimony<sup>3</sup> have been known to react with  $\alpha$ ,  $\beta$ -unsaturated ketones and aldehydes in the presence of a catalytic amount of Pd(II) salt to give the corresponding Michael-type hydroarylation compounds,  $\beta$ -aryl-substituted saturated ketones and aldehydes, respectively. Although there are several reports of transition metal [Rh(I),<sup>4a</sup> Cu(II)<sup>4b</sup>]-catalyzed Michael-type hydroarylation or hydroalkylation of nitroalkenes using organoborons and organozincs, examples that use a palladium salt as catalyst are quite rare.<sup>4c</sup> We have now examined carefully Pd(II)-catalyzed hydroarylation of nitroalkenes using several arylheteroatom compounds in acetic acid (AcOH) by taking the atom economy<sup>5</sup> of aryl groups into account and have found that aryl groups of aryltins and sodium tetraarylborates could be transferred quite effectively to the products,  $\beta$ -arylnitroalkanes. The addition of the salt of a Group 15 element, such as BiCl<sub>3</sub>, SbCl<sub>3</sub>, Bi<sub>2</sub>O<sub>3</sub> etc., in a catalytic amount much improved the product yield in this catalytic system in some cases. Details of the results of this Michael-type hydroarylation are reported here.<sup>6</sup>

### Results and Discussion

**Palladium(II)-Catalyzed Hydrophenylation of Nitroalkenes Using Tetraphenyltin.** At first, the catalytic system used so far for the hydroarylation reaction of  $\alpha$ ,  $\beta$ -unsaturated ketones and aldehydes with aryltin compounds was examined for use with nitroalkenes.<sup>2</sup> Thus,  $\beta$ -nitrostyrene (2-nitro-1-phenylethene, **1a**, 2 mmol) was treated with Ph<sub>4</sub>Sn (**2m**, 0.5 mmol, 0.25 molar amount to **1a**) in the presence of PdCl<sub>2</sub> (0.02 mmol, 0.01 molar amount to **1a**) and LiCl (4 mmol, 2 molar amounts to **1a**) in AcOH (20 mL) at 25 °C for 20 h. As a result, biphenyl (**4m**) was mainly obtained together with a Michael-type hydroarylated product, 2-nitro-1,1-diphenylethane (**3am**) (Scheme 1; Table 1, Entry 1). Unfortunately, the yield of **4m** much increased at a higher temperature (50 °C) without any improvement of the yield of **3am** (Table 1, Entries 1–4), unlike the case of the reaction using  $\alpha$ ,  $\beta$ -unsaturated ketones and aldehydes.<sup>2</sup>

A larger amount of PdCl<sub>2</sub> (0.1 mmol, 0.05 molar amount to **1a**) was needed for producing **3am** as a major product, where more than two phenyl groups of **2m** could be transferred to the hydroarylated product (Table 1, Entry 5). The presence of LiCl was necessary for this catalytic system to afford the hydroarylated product efficiently (Table 1, Entries 5 and 6). Instead of LiCl, the chlorides CaCl<sub>2</sub> and MgCl<sub>2</sub> were also effective as an additive (Table 1, Entries 7 and 8). The complex [PdCl<sub>2</sub>(PhCN)<sub>2</sub>] was as effective as PdCl<sub>2</sub> as a catalyst (Table 1, Entry 9), while [PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>], rhodium salts such as RhCl<sub>3</sub>·3H<sub>2</sub>O, [RhCl(CO)<sub>2</sub>]<sub>2</sub>, and [Rh<sub>3</sub>O(OAc)<sub>6</sub>(H<sub>2</sub>O)<sub>3</sub>]OAc, and copper salts such as CuCl<sub>2</sub>, Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O, CuCl, and CuI were revealed to be ineffective for this hydroarylation.

A similar treatment of other nitroalkenes bearing a substituent on the phenyl ring of **1a**, such as *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CH=CHNO<sub>2</sub> (**1b**), *p*-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>CH=CHNO<sub>2</sub> (**1c**), *p*-ClC<sub>6</sub>H<sub>4</sub>CH=CHNO<sub>2</sub> (**1d**), *p*-BrC<sub>6</sub>H<sub>4</sub>CH=CHNO<sub>2</sub> (**1e**), *m*-NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>CH=CHNO<sub>2</sub> (**1f**), and *o*-NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>CH=CHNO<sub>2</sub> (**1g**), afforded the corresponding hydroarylated products (**3bm**, **3cm**, **3dm**, **3em**, **3fm**, and **3gm**, respectively) in moderate to good yields (Scheme 1; Table 2, Entries 2–7), where no appreciable substituent effects were observed. From nitroalkenes having an alkyl group in place of an aryl group such as *n*-C<sub>7</sub>H<sub>15</sub>CH=CHNO<sub>2</sub> (**1h**) and *c*-C<sub>6</sub>H<sub>11</sub>CH=CHNO<sub>2</sub> (**1i**), the selectivity for the expected nitroalkane products became higher, sacrificing the formation of biphenyl (Table 2, Entries 8 and 9). The hydroarylation of  $\beta$ -substituted- $\alpha$ -nitroalkenes, which bear a bulky alkyl substituent or heteroaryl group at the  $\beta$ -carbon such as 3,3-dimethyl-1-nitro-1-butene [**1j**, (CH<sub>3</sub>)<sub>3</sub>CCH=CHNO<sub>2</sub>], 2-(2-nitroethenyl)thiophene (**1k**, 2-C<sub>4</sub>H<sub>3</sub>SCH=CHNO<sub>2</sub>), and 2-(2-nitroethenyl)furan (**1l**, 2-C<sub>4</sub>H<sub>3</sub>OCH=CHNO<sub>2</sub>), did not proceed well, biphenyl being the main product (Table 2, Entries 10–12). No hydroarylation occurred for  $\alpha$ ,  $\beta$ -disubstituted- $\alpha$ -nitroalkenes such as **5** and **6**, both having a substituent on the same carbon atom where a nitro group is present, probably due to the steric hindrance at



Scheme 1. Hydroarylation of nitroalkenes

Table 1. Pd(II)-Catalyzed Hydrophenylation of  $\beta$ -Nitrostyrene (**1a**) Using Ph<sub>4</sub>Sn (**2m**)<sup>a)</sup>

| Entry           | Pd catalyst/mmol                         |      | Additive/mmol     |   | Isolated yield/% <sup>b)</sup> |    |
|-----------------|------------------------------------------|------|-------------------|---|--------------------------------|----|
|                 |                                          |      |                   |   | 3am                            | 4m |
| 1               | PdCl <sub>2</sub>                        | 0.02 | LiCl              | 4 | 14                             | 23 |
| 2 <sup>c)</sup> | PdCl <sub>2</sub>                        | 0.02 | LiCl              | 4 | 12                             | 45 |
| 3               | PdCl <sub>2</sub>                        | 0.04 | LiCl              | 4 | 30                             | 32 |
| 4 <sup>d)</sup> | PdCl <sub>2</sub>                        | 0.04 | LiCl              | 4 | 12                             | 48 |
| 5               | PdCl <sub>2</sub>                        | 0.1  | LiCl              | 4 | 52                             | 39 |
| 6               | PdCl <sub>2</sub>                        | 0.1  | —                 | — | 5                              | 15 |
| 7               | PdCl <sub>2</sub>                        | 0.1  | CaCl <sub>2</sub> | 2 | 46                             | 31 |
| 8               | PdCl <sub>2</sub>                        | 0.1  | MgCl <sub>2</sub> | 2 | 45                             | 33 |
| 9               | [PdCl <sub>2</sub> (PhCN) <sub>2</sub> ] | 0.1  | LiCl              | 4 | 52                             | 31 |

a) Reaction conditions: **1a** (2 mmol) and **2m** (0.5 mmol) in AcOH (20 mL) at 25 °C for 20 h. b) Based on **2m**: 2 mmol of **3am** and 1 mmol of biphenyl (**4m**) correspond to 100% yield, respectively. c) At 50 °C for 5 h. d) At 50 °C for 2 h.

the aryllpalladation step (see “Plausible Reaction Scheme”). The application of this reaction to **7**, which could be regarded as a  $\beta$ ,  $\beta$ -disubstituted- $\alpha$ -nitroalkene, resulted in the major formation of biphenyl (**4m**) together with a small amount of a complex mixture which contained little of the corresponding expected hydroarylated product.

It is worth noting that this type of catalytic reaction could not be applied to such Michael-type acceptors as  $\alpha$ ,  $\beta$ -unsaturated esters and nitriles.

**Palladium(II)-Catalyzed Hydroarylation of  $\beta$ -Nitrostyrene Using Other Arylating Reagents.** The hydroarylation of **1a** with some tetraaryltins was next investigated using the above catalytic system. Thus, **1a** (2 mmol) was treated with Ar<sub>4</sub>Sn (0.5 mmol) in the presence of PdCl<sub>2</sub> (0.1 mmol) and LiCl (4 mmol) in AcOH (20 mL) at 25 °C for 20 h. As a result, the hydroarylation with (*p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)<sub>4</sub>Sn (**2n**) was revealed to be more efficient than that with Ph<sub>4</sub>Sn (**2m**), afford-

ing a larger amount of the Michael-type hydroarylated product (**3an** = **3bm**) together with a smaller amount of biaryl (**4n**) (Table 3, Entry 2). On the contrary, biaryl **4o** was obtained as the main product in the case of (*p*-ClC<sub>6</sub>H<sub>4</sub>)<sub>4</sub>Sn (**2o**) (Table 3, Entry 3). Arylating reagents other than tetraaryltins were also investigated: these include Ph<sub>3</sub>SnCl (**2p**), Ph<sub>2</sub>SnCl<sub>2</sub> (**2q**), Ph<sub>4</sub>Ge, Ph<sub>3</sub>Sb, Ph<sub>3</sub>Sb(OAc)<sub>2</sub>, Ph<sub>3</sub>Bi, Ph<sub>3</sub>Bi(OAc)<sub>2</sub>, PhB(OH)<sub>2</sub>, NaBPh<sub>4</sub> (**2r**), and NaB(*p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)<sub>4</sub> (**2s**). Thus, one molar amount of **1a** was treated with one molar amount of arylating reagent as aryl group(s) (i.e., a quarter molar amount of Ph<sub>4</sub>Ge, one third molar amount of **2p**, Ph<sub>3</sub>Sb, Ph<sub>3</sub>Sb(OAc)<sub>2</sub>, Ph<sub>3</sub>Bi, Ph<sub>3</sub>Bi(OAc)<sub>2</sub>, **2r**, and **2s**, a half molar amount of **2q**, and one molar amount of PhB(OH)<sub>2</sub>, respectively) in the presence of PdCl<sub>2</sub> (0.05 molar amount) and LiCl (2 molar amounts) in AcOH at 25 °C for 20 h. Among these reagents, **2q** and **2r** mainly afforded the Michael-type hydroarylated product **3am** together with a small amount of biphenyl (**4m**), phenyl groups

Table 2. Pd(II)-Catalyzed Hydrophenylation of Nitroalkenes (1) Using Ph<sub>4</sub>Sn (2m)<sup>a)</sup>

| Entry           | 1  | Isolated yield/% <sup>b)</sup> |    |
|-----------------|----|--------------------------------|----|
|                 |    | 3                              | 4m |
| 1 <sup>c)</sup> | 1a | 3am, 52                        | 39 |
| 2               | 1b | 3bm, 59                        | 31 |
| 3               | 1c | 3cm, 50                        | 33 |
| 4               | 1d | 3dm, 50                        | 43 |
| 5               | 1e | 3em, 53                        | 35 |
| 6               | 1f | 3fm, 37                        | 36 |
| 7               | 1g | 3gm, 50                        | 47 |
| 8               | 1h | 3hm, 68                        | 13 |
| 9               | 1i | 3im, 54                        | 9  |
| 10              | 1j | 3jm, 6                         | 75 |
| 11              | 1k | 3km, 24                        | 51 |
| 12              | 1l | 3lm, 3                         | 27 |

a) Reaction conditions: **1** (1 mmol), **2m** (0.25 mmol), PdCl<sub>2</sub> (0.05 mmol), and LiCl (2 mmol) in AcOH (10 mL) at 25 °C for 20 h. b) Based on **2m**: 1 mmol of **3** and 0.5 mmol of biphenyl (**4m**) correspond to 100% yield, respectively. c) Double scale reaction.

Table 3. Pd(II)-Catalyzed Hydrophenylation of  $\beta$ -Nitrostyrene (1a) Using Various Arylating Reagents (2)<sup>a)</sup>

| Entry           | 2/mmol  | Isolated yield/% <sup>b)</sup> |        |
|-----------------|---------|--------------------------------|--------|
|                 |         | 3                              | 4      |
| 1               | 2m 0.5  | 3am, 52                        | 4m, 39 |
| 2               | 2n 0.5  | 3an, 67                        | 4n, 19 |
| 3               | 2o 0.5  | 3ao, 13                        | 4o, 71 |
| 4               | 2p 0.67 | 3am, 39                        | 4m, 44 |
| 5               | 2q 1.0  | 3am, 70                        | 4m, 19 |
| 6               | 2r 0.67 | 3am, 59                        | 4m, 12 |
| 7 <sup>c)</sup> | 2s 0.33 | 3an, 19                        | 4n, 3  |

a) Reaction conditions: **1a** (2 mmol), PdCl<sub>2</sub> (0.1 mmol), and LiCl (4 mmol) in AcOH (20 mL) at 25 °C for 20 h. b) Based on **2**; 2 mmol as Ar group: 2 mmol of **3** and 1 mmol of biaryl (**4**) correspond to 100% yield, respectively. c) Half scale reaction.

being transferred more efficiently to **1a** than those of **2m** (Table 3, Entries 5 and 6). In the case of Ph<sub>3</sub>Bi and Ph<sub>3</sub>Bi(OAc)<sub>2</sub>, **4m** was formed almost exclusively. During the treatment of **2q** in the presence of PdCl<sub>2</sub> and LiCl, the reaction mixture turned from orange solution to yellow turbid solution, where the complexation might occur. Unexpectedly, both **2p** and **2s** were not so active as an arylating reagent in this catalytic system (Table 3, Entries 4 and 7). The reagent Ph<sub>3</sub>Sb(OAc)<sub>2</sub> scarcely reacted with **1a**. In this catalytic system, the reagent PhB(OH)<sub>2</sub> was quite inactive, unlike the catalytic system reported by Hayashi and co-workers.<sup>7</sup>

Arylating reagents such as **2n**, **2q**, and **2r** were next treated with several other nitroalkenes in this catalytic system. The typical results are listed in Table 4. The hydroarylation of  $\beta$ -nitrostyrene derivatives (**1b–1f**) using these reagents proceeded as effectively as that of **1a**, but no substituent effect was clearly revealed (Table 4, Entries 1, 2, 7, 8, 12, and 13). The hydroarylation was also applicable to nitroalkenes **1h** and **1i** (Table 4, Entries 3, 4, 9, 10, and 14), where little biaryl for-

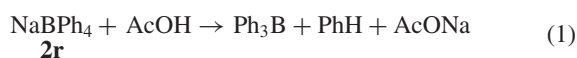
Table 4. Pd(II)-Catalyzed Hydrophenylation of Nitroalkenes (1) Using Various Arylating Reagents (2)<sup>a)</sup>

| Entry | 2/mmol  | 1  | Isolated yield/% <sup>b)</sup> |        |
|-------|---------|----|--------------------------------|--------|
|       |         |    | 3                              | 4      |
| 1     | 2n 0.25 | 1b | 3bn, 63                        | 4n, 24 |
| 2     | 2n 0.25 | 1e | 3en, 67                        | 4n, 20 |
| 3     | 2n 0.25 | 1h | 3hn, 43                        | 4n, 3  |
| 4     | 2n 0.25 | 1i | 3in, 42                        | 4n, 3  |
| 5     | 2n 0.25 | 1k | 3kn, 35                        | 4n, 37 |
| 6     | 2n 0.25 | 1l | 3ln, 22                        | 4n, 50 |
| 7     | 2q 0.5  | 1b | 3bm, 66                        | 4m, 18 |
| 8     | 2q 0.5  | 1f | 3fm, 37                        | 4m, 16 |
| 9     | 2q 0.5  | 1h | 3hm, 72                        | 4m, 3  |
| 10    | 2q 0.5  | 1i | 3im, 66                        | 4m, 9  |
| 11    | 2q 0.5  | 1k | 3km, 45                        | 4m, 33 |
| 12    | 2r 0.33 | 1c | 3cm, 61                        | 4m, 12 |
| 13    | 2r 0.33 | 1d | 3dm, 62                        | 4m, 20 |
| 14    | 2r 0.33 | 1h | 3hm, 49                        | 4m, 10 |
| 15    | 2r 0.33 | 1k | 3km, 52                        | 4m, 16 |

a) Reaction conditions: **1** (1 mmol), PdCl<sub>2</sub> (0.05 mmol), and LiCl (2 mmol) in AcOH (10 mL) at 25 °C for 20 h. b) Based on **2**; 1 mmol as Ar group: 1 mmol of **3** and 0.5 mmol of biaryl (**4**) correspond to 100% yield, respectively.

mation occurs. Nitroalkenes **1k** and **1l** could also be used (Table 4, Entries 5, 6, 11, and 15), but no reaction occurred with nitroalkenes **5** and **6**.

It has been well known<sup>1c</sup> that **2r** partly decomposes in AcOH as shown in Eq. 1 to produce triphenylborane and benzene, indicating that one of the four phenyl groups is wasted. Therefore, the hydroarylation was also carried out in other solvents such as



tetrahydrofuran (THF) and ethanol (EtOH), hoping to utilize all phenyl groups. However, little of the expected product **3am** was obtained in these solvents even when several basic inorganic salts such as NaOAc, Li<sub>2</sub>CO<sub>3</sub>, LiOH·H<sub>2</sub>O, and LiOAc were added in order to make transmetalation of phenyl groups more efficient.<sup>5c</sup>

**The Effect of Added Lewis Acid.** Since it has been found that the presence of antimony(III) chloride (SbCl<sub>3</sub>) was effective for the Michael-type hydroarylation of  $\alpha,\beta$ -unsaturated carbonyl compounds using sodium tetraarylborates and arylboronic acids in AcOH,<sup>1b,c</sup> the effect of Lewis acid upon the reaction between **1a** and Ph<sub>4</sub>Sn (**2m**) was next examined. The treatment of **1a** (1 mmol) with **2m** (0.25 mmol, 0.25 molar amount to **1a**) in the presence of PdCl<sub>2</sub> (0.05 mmol, 0.05 molar amount to **1a**), LiCl (2 mmol, 2 molar amounts to **1a**), and SbCl<sub>3</sub> (0.1 mmol, 0.1 molar amount to **1a**) in AcOH (10 mL) at 25 °C for 20 h afforded **3am** in a quite high yield together with a diminishing amount of biphenyl (**4m**), where more than three out of four phenyl groups of **1a** were transferred to the hydroarylated product (Table 5, Entry 1). This catalytic hydroarylation reaction was then carried out in the presence of a Lewis acid other than SbCl<sub>3</sub>, such as SbOCl, Sb<sub>2</sub>O<sub>3</sub>, BiCl<sub>3</sub>, Bi<sub>2</sub>O<sub>3</sub>, Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O, Bi(OTf)<sub>3</sub>, BF<sub>3</sub>·OEt<sub>2</sub>, AlCl<sub>3</sub>, or InCl<sub>3</sub>.



Table 6. Hydrophenylation of Nitroalkenes Using Ar<sub>4</sub>Sn (2) in the Presence of BiCl<sub>3</sub><sup>a)</sup>

| Entry | 1  | 2  | Isolated yield/% <sup>b)</sup> |             |
|-------|----|----|--------------------------------|-------------|
|       |    |    | 3                              | 4           |
| 1     | 1a | 2m | 3am, 83 (52)                   | 4m, 16 (39) |
| 2     | 1a | 2n | 3an, 76 (67)                   | 4n, 17 (19) |
| 3     | 1b | 2m | 3bm, 82 (59)                   | 4m, 10 (31) |
| 4     | 1c | 2m | 3cm, 81 (50)                   | 4m, 15 (33) |
| 5     | 1d | 2m | 3dm, 88 (50)                   | 4m, 6 (43)  |
| 6     | 1e | 2m | 3em, 85 (53)                   | 4m, 13 (35) |
| 7     | 1f | 2m | 3fm, 77 (37)                   | 4m, 16 (36) |
| 8     | 1g | 2m | 3gm, 55 (50)                   | 4m, 28 (47) |
| 9     | 1h | 2m | 3hm, 78 (68)                   | 4m, 3 (13)  |
| 10    | 1i | 2m | 3im, 80 (54)                   | 4m, 1 (9)   |
| 11    | 1j | 2m | 3jm, 5 (6)                     | 4m, 70 (75) |
| 12    | 1k | 2m | 3km, 25 (24)                   | 4m, 39 (51) |
| 13    | 1l | 2m | 3lm, 7 (3)                     | 4m, 21 (27) |

a) Reaction conditions: **1** (1 mmol), **2** (0.25 mmol), PdCl<sub>2</sub> (0.05 mmol), LiCl (2 mmol), and BiCl<sub>3</sub> (0.1 mmol) in AcOH (10 mL) at 25 °C for 20 h. b) Based on **2**: 1 mmol of **3** and 0.5 mmol of biaryl (**4**) correspond to 100% yield, respectively. The yields obtained in the absence of BiCl<sub>3</sub> are shown in parentheses.

11–13), showing that the addition of BiCl<sub>3</sub> does not always make the hydroarylation more efficient. No hydroarylation occurred to **5** or **6** even in the presence of BiCl<sub>3</sub> or SbCl<sub>3</sub>. In the case of **7**, a complex mixture was obtained whether BiCl<sub>3</sub> is present or not.

**Plausible Reaction Scheme.** Although the details are not yet known, Scheme 2 is proposed for this catalytic Michael-type addition reaction using organotin compounds as an example. The transmetalation of Sn(IV) moiety of aryltin(IV) compounds by Pd(II) (**A**) occurs to give an Ar–Pd(II)–X (X = OAc or Cl) species (**B**), which adds to nitroalkenes to afford an alkylpalladium(II) species (**C**).<sup>10</sup> The Pd(II) species **C** might be in equilibrium with a palladium(II) nitronate (**D**) to which the other organotin(IV) compound attacks to afford a tin(IV) nitronate (**E**), regenerating the Ar–Pd(II)–X species. The species **E** is hydrolyzed (solvolized) to lead to the hydroarylated product. A similar reaction scheme has already been proposed in the reaction between the corresponding Rh enolate and arylboron compounds.<sup>11</sup> The role of metal chloride (mainly LiCl) is to make a Pd(II) salt soluble and also to make the transmetalation step more facile by coordination to aryltin(IV) compounds.<sup>12</sup> In the presence of the salt of a Group 15 element, such as BiCl<sub>3</sub>, SbCl<sub>3</sub>, and Bi<sub>2</sub>O<sub>3</sub> [abbreviated as PnX<sub>3</sub>: it is assumed that Bi<sub>2</sub>O<sub>3</sub> turns to Bi(OAc)<sub>3</sub> or Bi(O)OAc in AcOH], the salt may coordinate to the oxygen atom of the nitro group of nitroalkenes. Then the carbopalladation occurs to give the species **F**, from which a Pd(II) species is eliminated to give a Group 15 nitronate (**G**). In the cases of **1j**, **5**, **6**, and **7**, the substituent at the carbon atom where a nitro and/or alkyl group attaches might prevent the attack of the species **B** to the alkenic part, although the exact reason is not yet known. For the formation of biaryl, the second transmetalation of Sn(IV) moiety of aryltin(IV) compounds by the species **B** occurs to give Ar–Pd(II)–Ar species, followed by the reductive elimination.

## Experimental

**General.** Melting points were determined on a Yanaco MP-J3 micro melting point apparatus and are uncorrected. The <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded with JEOL JNM-AL300 spectrometer for solutions in CDCl<sub>3</sub> with Me<sub>4</sub>Si as an internal standard. Chemical shifts are reported in δ ppm units downfield from Me<sub>4</sub>Si. High resolution mass spectra (FAB HRMS) were obtained with a JEOL JMX-SX 102A spectrometer. The isolation of a pure product was carried out by column chromatography on SiO<sub>2</sub> (Merck 60, 230–400 mesh, Merck KGaA.).

**Materials.** Solvents except AcOH and EtOH were freshly distilled under N<sub>2</sub> prior to use; tetrahydrofuran (THF) was distilled from sodium diphenylketyl; C<sub>6</sub>H<sub>6</sub> and CH<sub>2</sub>Cl<sub>2</sub> were distilled from calcium hydride. Nitroalkenes such as **1b**, **1c**, **1d**, **1e**, **1f**, **1h**, **1i**, **1j**, and **7** were prepared from the corresponding carbonyl compounds and nitromethane in the presence of NaOH, KOH, or NaOMe in MeOH according to the literature procedure,<sup>13</sup> typical physical data being shown below. Other nitroalkenes such as **1a**, **1g**, **1k**, **1l**, **5**, and **6** are commercial products. The palladium complexes such as [PdCl<sub>2</sub>(PhCN)<sub>2</sub>]<sup>14a</sup> and [PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>]<sup>14b</sup> were prepared by the literature methods. The compound [Rh<sub>3</sub>O(OAc)<sub>6</sub>(H<sub>2</sub>O)<sub>3</sub>]OAc was prepared by the literature method from RhCl<sub>3</sub>·3H<sub>2</sub>O and AgOAc in aqueous AcOH.<sup>14c</sup> Lithium acetate was prepared from LiOH·H<sub>2</sub>O and acetic anhydride under reflux, followed by evaporation of unreacted acetic anhydride. Commercially available chlorides such as MgCl<sub>2</sub>, SbCl<sub>3</sub>, and BiCl<sub>3</sub> were dehydrated by thionyl chloride and dried under vacuum prior to use. Arylating reagents such as **2m**, **2p**, **2q**, **2r**, **2s**, Ph<sub>4</sub>Ge, Ph<sub>3</sub>Sb, and PhB(OH)<sub>2</sub> are commercial products. Tetraaryltins such as **2n** and **2o** were prepared from the corresponding Grignard reagents and SnCl<sub>4</sub> (as C<sub>6</sub>H<sub>6</sub> solution) in THF, followed by recrystallization.<sup>2,15</sup> Triphenylbismuthine (Ph<sub>3</sub>Bi) was prepared from phenylmagnesium bromide and BiCl<sub>3</sub>, followed by recrystallization from petroleum ether.<sup>16</sup> Bismuth triflate [Bi(OTf)<sub>3</sub>] was prepared from trifluoromethanesulfonic acid and Ph<sub>3</sub>Bi,<sup>17</sup> and used without further purification. The compounds such as Ph<sub>3</sub>Sb(OAc)<sub>2</sub><sup>18</sup> and Ph<sub>3</sub>Bi(OAc)<sub>2</sub><sup>16</sup> were prepared by the literature methods, using CH<sub>2</sub>Cl<sub>2</sub> as solvent.

**p-Methyl-β-nitrostyrene (1b):** Recrystallized from hexane–toluene, mp 101–102 °C (lit. 102 °C,<sup>19</sup> 103–103.5 °C<sup>20</sup>); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 2.41 (s, 3H), 7.24–7.27 (d, *J* = 8.0 Hz, 2H), 7.43–7.46 (d, *J* = 8.0 Hz, 2H), 7.54–7.59 (d, *J* = 13.6 Hz, 1H), 7.96–8.02 (d, *J* = 13.6 Hz, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) δ 21.66, 127.27, 129.18, 130.13, 136.29, 139.17, 143.09.

**p-Methoxy-β-nitrostyrene (1c):** Recrystallized from hexane–benzene, mp 85.5–87.5 °C (lit. 90 °C,<sup>21</sup> 86 °C,<sup>22</sup> 86–87 °C,<sup>23,24</sup>); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 3.87 (s, 3H), 6.94–6.98 (d, *J* = 8.6 Hz, 2H), 7.49–7.55 (d, *J* = 8.6 Hz, 2H and d, *J* = 13.7 Hz, 1H), 7.95–8.01 (d, *J* = 13.7 Hz, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) δ 55.52, 114.91, 122.54, 131.15, 135.03, 139.01, 162.93.

**p-Chloro-β-nitrostyrene (1d):** Recrystallized from toluene, mp 111–113 °C (lit. 111–112 °C,<sup>25</sup> 112–112.5 °C,<sup>23</sup> 113–114 °C<sup>26,27</sup>); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 7.41–7.51 (m, 4H), 7.53–7.59 (d, *J* = 13.8 Hz, 1H), 7.94–7.99 (d, *J* = 13.8 Hz, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) δ 128.51, 129.76, 130.24, 137.40, 137.66, 138.31.

**p-Bromo-β-nitrostyrene (1e):** Recrystallized from toluene, mp 151–153 °C (lit. 150.5–151 °C,<sup>27</sup> 156–158 °C<sup>28</sup>); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 7.39–7.44 (d, *J* = 8.6 Hz, 2H), 7.55–7.63 (d, *J* = 13.7 Hz, 1H and d, *J* = 8.6 Hz, 2H), 7.92–7.97 (d, *J* =

13.7 Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  126.77, 128.93, 130.37, 132.73, 137.45, 137.75.

***m*,*β*-Dinitrostyrene (1f):** Recrystallized from ethyl acetate, mp 124.5–126 °C (lit. 124.5–125.5 °C<sup>23</sup>);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  7.64–7.71 (t,  $J$  = 8.0 Hz, 1H and d,  $J$  = 13.8 Hz, 1H), 7.85–7.89 (d,  $J$  = 8.0 Hz, 1H), 8.03–8.08 (d,  $J$  = 13.8 Hz, 1H), 8.34–8.38 (d,  $J$  = 8.0 Hz, 1H), 8.42 (s, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  123.47, 126.21, 130.61, 131.82, 134.41, 136.22, 139.28, 148.83.

**1-Nitro-1-nonene (1h):** Obtained as pale yellow oil, bp 150 °C (bath temp., 5 mmHg, 1 mmHg = 133.322 Pa) (lit. 91–95 °C/0.2–0.3 mmHg<sup>29</sup>);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  0.86–0.92 (t,  $J$  = 6.7 Hz, 3H), 1.20–1.44 (m 8H), 1.46–1.55 (quartet-d,  $J$  = 7.3, 1.5 Hz, 2H), 2.23–2.31 (quartet,  $J$  = 7.3 Hz, 2H), 6.95–7.01 (dt,  $J$  = 13.4, 1.5 Hz, 1H), 7.23–7.33 (dt,  $J$  = 13.4, 7.3 Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  13.95, 22.51, 27.65, 28.37, 28.84, 28.98, 31.57, 139.47, 142.78.

**(2-Nitroethenyl)cyclohexane (1i):** Obtained as pale yellow oil, bp 115–120 °C (bath temp., 6 mmHg) (lit. 100 °C/0.4 mmHg<sup>30</sup>);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  1.14–1.41 (m, 5H), 1.69–1.84 (m 5H), 2.21–2.32 (m, 1H), 6.91–6.96 (dd,  $J$  = 13.5, 0.9 Hz, 2H), 7.18–7.29 (dd,  $J$  = 13.5, 7.1 Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  25.20, 25.37, 31.16, 37.27, 138.02, 147.03.

**3,3-Dimethyl-1-nitro-1-butene (1j):** Obtained as pale yellow oil, bp 70 °C (bath temp., 7 mmHg) (lit. 40 °C/2 mmHg<sup>31</sup>);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  1.17 (s, 9H), 6.88–6.93 (d,  $J$  = 13.6 Hz, 1H), 7.24–7.30 (d,  $J$  = 13.6 Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  28.21, 32.47, 137.01, 151.76.

**(Nitromethylene)cyclohexane (7):** Obtained as yellow oil, bp 100–130 °C (bath temp., 6 mmHg) (lit. 50–52 °C/0.2 mmHg,<sup>32</sup> 83 °C/3 mmHg<sup>33</sup>);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  1.61–1.78 (m, 6H), 2.19–2.24 (t,  $J$  = 6.0 Hz, 2H), 2.83–2.88 (t,  $J$  = 6.0 Hz, 2H), 6.92 (s, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  25.59, 27.14, 28.05, 28.72, 34.18, 132.08, 155.65.

**Tetra(*p*-tolyl)tin (2n):** Recrystallized from benzene–ethyl acetate, mp 242–242.5 °C (lit. 238 °C<sup>15c</sup>);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  2.35 (s, 12H), 7.18–7.21 (d,  $J$  = 7.8 Hz, 8H), 7.45–7.49 (d,  $J$  = 7.8 Hz, 8H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  21.48, 129.38, 134.42, 137.15, 138.76.

**Tetrakis(*p*-chlorophenyl)tin (2o):** Recrystallized from benzene–petroleum ether, mp 198–201 °C (lit. 199 °C<sup>15c</sup>);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  7.36–7.58 (m, 16H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  129.19, 134.62, 136.26, 138.09.

**General Procedure for Palladium(II)-Catalyzed Michael-Type Addition Using Aryltin Compounds (for Example, Table 1, Entry 5).** A mixture of  $\text{PdCl}_2$  (0.018 g, 0.10 mmol), LiCl (0.170 g, 4.01 mmol), and AcOH (5 mL) was stirred to give a homogeneous red solution. To this solution,  $\beta$ -nitrostyrene (**1a**), 0.298 g, 2.00 mmol), tetraphenyltin (**2m**, 0.214 g, 0.501 mmol), and AcOH (15 mL) were added and the resulting mixture was stirred at 25 °C. After stirring for 20 h, the mixture was poured into brine (150 mL) and extracted with diethyl ether or ethyl acetate (30 mL  $\times$  5). The organic layer was washed with dilute HCl (ca. 3 mol·dm<sup>−3</sup>, 30 mL  $\times$  3), water (30 mL  $\times$  2), and saturated  $\text{NaHCO}_3$  solution (usually 50 mL  $\times$  2) and then dried over anhydrous  $\text{MgSO}_4$ . After removal of the solvent under reduced pressure, the brownish yellow residue was subjected to column chromatography to give biphenyl (**4m**, 0.061 g, 0.392 mmol, 39.1% yield) and 2-nitro-1,1-diphenylethane (**3am**, 0.239 g, 1.05 mmol, 52.4% yield).

**General Procedure for Palladium(II)-Catalyzed Michael-Type Addition Using Aryltin Compounds in the Presence of**

**$\text{Sb}_2\text{O}_3$  or  $\text{Bi}_2\text{O}_3$  (for Example, Table 5, Entry 8).** A mixture of  $\text{PdCl}_2$  (0.009 g, 0.05 mmol), LiCl (0.085 g, 2.0 mmol),  $\text{Bi}_2\text{O}_3$  (0.023 g, 0.049 mmol), and AcOH (1 mL) was stirred to give a homogeneous red solution. To this solution, **1a** (0.149 g, 0.999 mmol), **2m** (0.107 g, 0.250 mmol), and AcOH (9 mL) were added. After stirring for 20 h, the mixture was similarly treated as described above to afford **4m** (0.0118 g, 0.0765 mmol, 15.3% yield) and **3am** (0.193 g, 0.848 mmol, 84.8% yield).

**General Procedure for Palladium(II)-Catalyzed Michael-Type Addition Using Aryltin Compounds in the Presence of Some Other Additive (for Example, Table 5, Entry 4).** To a homogeneous red solution which consisted of  $\text{PdCl}_2$  (0.009 g, 0.05 mmol), LiCl (0.085 g, 2.0 mmol), and AcOH (1 mL), **1a** (0.149 g, 0.999 mmol), **2m** (0.107 g, 0.250 mmol),  $\text{BiCl}_3$  (0.032 g, 0.101 mmol), and AcOH (9 mL) were added successively and the resulting mixture was stirred for 20 h. The mixture was then treated as above to afford **4m** (0.0122 g, 0.0791 mmol, 15.8% yield) and **3am** (0.188 g, 0.829 mmol, 82.9% yield).

The physical data of the produced hydroarylated compounds are shown below in which **3em**, **3en**, **3fm**, **3gm**, **3hm**, **3hn**, **3im**, **3in**, **3jm**, **3km**, **3kn**, **3lm**, and **3ln** are new compounds.

**2-Nitro-1,1-diphenylethane (3am):** Obtained as pale yellow oil (lit. mp 68–70 °C,<sup>34</sup> 69–70 °C<sup>35</sup>);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  4.81–4.91 (m, 3H), 7.16–7.28 (m, 10H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  48.88, 79.16, 127.53, 127.60, 128.96, 139.15.

**2-Nitro-1-phenyl-1-(*p*-tolyl)ethane (3an = 3bm):** Obtained as pale yellow oil (lit. mp 47–48 °C<sup>35</sup>);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  2.27 (s, 3H), 4.79–4.91 (m, 3H), 7.08–7.10 (m, 4H), 7.14–7.29 (m, 5H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  20.94, 48.57, 79.22, 127.43, 127.48, 127.57, 128.93, 129.64, 136.23, 137.20, 139.47.

**1-(4-Chlorophenyl)-2-nitro-1-phenylethane (3ao = 3dm):** Obtained as pale yellow oil (lit. mp 67–68 °C<sup>35</sup>);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  4.82–4.86 (m, 3H), 7.07–7.30 (m, 9H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  48.01, 78.58, 127.32, 127.51, 128.84, 128.88, 133.10, 137.65, 138.57.

**2-Nitro-1,1-di(*p*-tolyl)ethane (3bn):** Obtained as pale yellow oil (lit. bp 162 °C/0.4 mmHg<sup>35</sup>);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  2.22 (s, 6H), 4.74–4.83 (m, 3H), 7.03–7.06 (m, 8H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  20.78, 48.10, 79.15, 127.31, 129.47, 136.38, 136.93.

**1-(*p*-Methoxyphenyl)-2-nitro-1-phenylethane (3cm):** Obtained as yellow oil (lit. bp 166–168 °C/0.4 mmHg<sup>35</sup>);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  3.68 (s, 3H), 4.63–5.10 (m, 3H), 6.79–6.82 (d,  $J$  = 7.7 Hz, 2H), 7.09–7.12 (d,  $J$  = 7.7 Hz, 2H), 7.16–7.29 (m, 5H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  48.04, 54.99, 79.17, 114.18, 127.26, 127.38, 128.55, 128.77, 131.09, 139.46, 158.72.

**1-(*p*-Bromophenyl)-2-nitro-1-phenylethane (3em):** Obtained as pale yellow oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  4.76–4.87 (m, 3H), 7.03–7.06 (d,  $J$  = 7.9 Hz, 2H), 7.13–7.31 (m, 5H), 7.34–7.38 (d,  $J$  = 7.9 Hz, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  48.06, 78.51, 121.27, 127.32, 127.53, 128.89, 129.18, 131.84, 138.13, 138.45. Found: C, 55.04; H, 4.11; N, 4.38%. Calcd for  $\text{C}_{14}\text{H}_{12}\text{BrNO}_2$ : C, 54.92; H, 3.95; N, 4.58%.

**1-(*p*-Bromophenyl)-2-nitro-1-(*p*-tolyl)ethane (3en):** Obtained as pale yellow oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  2.22 (s, 3H), 4.57–4.82 (m, 3H), 7.00–7.05 (m, 6H), 7.32–7.35 (d,  $J$  = 7.3 Hz, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  20.81, 47.82, 78.67, 121.23, 127.25, 129.18, 129.62, 131.86, 135.51, 137.28, 138.45. Found: C, 56.15; H, 4.42; N, 4.14%. Calcd for  $\text{C}_{15}\text{H}_{14}\text{BrNO}_2$ : C, 56.27; H, 4.41; N, 4.37%.

**2-Nitro-1-(*m*-nitrophenyl)-1-phenylethane (3fm):** Obtained as pale yellow viscous oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  5.03–5.12 (m, 3H), 7.23–7.32 (m, 5H), 7.38–7.44 (t,  $J = 7.8$  Hz, 1H), 7.58–7.62 (d,  $J = 7.5$  Hz, 1H), 8.00–8.04 (d,  $J = 7.7$  Hz, 1H), 8.14 (s, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  48.45, 78.39, 122.60, 127.66, 128.08, 129.32, 130.09, 134.05, 138.01, 138.14, 141.58, 148.47. HRMS (FAB) found: 273.0880. Calcd for  $\text{C}_{14}\text{H}_{13}\text{N}_2\text{O}_4$  ( $\text{M} + \text{H}^+$ ): 273.0875.

**2-Nitro-1-(*o*-nitrophenyl)-1-phenylethane (3gm):** Obtained as pale yellow viscous oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  4.94–5.11 (dd + dd,  $J = 7.9$ , 13.6 Hz, 2H), 5.58–5.65 (t,  $J = 8.0$  Hz, 1H), 7.20–7.32 (m, 5H), 7.34–7.43 (m, 2H), 7.50–7.56 (t,  $J = 7.6$  Hz, 1H), 7.81–7.85 (d,  $J = 8.1$  Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  42.83, 77.76, 125.10, 127.64, 127.80, 128.45, 128.96, 129.00, 133.16, 133.32, 137.24, 149.29. HRMS (FAB) found: 273.0873. Calcd for  $\text{C}_{14}\text{H}_{13}\text{N}_2\text{O}_4$  ( $\text{M} + \text{H}^+$ ): 273.0875.

**1-Nitro-2-phenylnonane (3hm):** Obtained as pale yellow oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  0.82–0.88 (t,  $J = 6.7$  Hz, 3H), 1.00–1.45 (m, 10H), 1.63–1.71 (quartet,  $J = 7.1$  Hz, 2H), 3.38–3.49 (quintet,  $J = 7.6$  Hz, 1H), 4.48–4.60 (dd + dd,  $J = 12.1$ , 7.5 Hz, 2H), 7.16–7.36 (m, 5H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  14.00, 22.54, 26.84, 28.96, 29.22, 31.68, 32.97, 44.34, 80.98, 127.47, 128.85, 139.54, 142.79. Found: C, 71.99; H, 9.58; N, 5.43%. Calcd for  $\text{C}_{15}\text{H}_{23}\text{NO}_2$ : C, 72.25; H, 9.30; N, 5.62%.

**1-Nitro-2-*p*-tolylnonane (3hn):** Obtained as yellow oil, bp 195 °C/1 mmHg (bath temp);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  0.82–0.88 (t,  $J = 6.8$  Hz, 3H), 1.05–1.40 (m, 10H), 1.61–1.69 (quartet,  $J = 7.2$  Hz, 2H), 2.32 (s, 3H), 3.34–3.45 (quintet,  $J = 7.6$  Hz, 1H), 4.45–4.58 (dd + dd,  $J = 16.2$ , 7.7 Hz, 2H), 7.04–7.08 (d,  $J = 8.1$  Hz, 2H), 7.12–7.15 (d,  $J = 8.1$  Hz, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  14.01, 21.02, 22.56, 26.87, 28.98, 29.26, 31.70, 32.99, 44.00, 81.15, 127.33, 129.54, 136.46, 137.11. Found: C, 73.20; H, 9.76; N, 5.03%. Calcd for  $\text{C}_{16}\text{H}_{25}\text{NO}_2$ : C, 72.96; H, 9.57; N, 5.32%.

**(2-Nitro-1-phenylethyl)cyclohexane (3im):** Obtained as pale yellow solid (from column chromatography), white crystal (recrystallized from hexane), mp 65–66.5 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  0.79–1.28 (m, 5H), 1.44–1.67 (m, 4H), 1.74–1.83 (m, 2H), 3.22–3.31 (ddd,  $J = 12.3$ , 9.9, 5.7 Hz, 1H), 4.57–4.66 (dd,  $J = 12.3$ , 9.9 Hz, 1H), 4.75–4.82 (dd,  $J = 12.3$ , 5.7 Hz, 1H), 7.11–7.15 (d,  $J = 8.1$  Hz, 2H), 7.23–7.34 (m, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  26.02, 26.03, 26.08, 30.50, 30.91, 40.83, 50.18, 78.79, 127.29, 128.09, 128.49, 138.75. Found: C, 72.12; H, 8.06; N, 5.94%. Calcd for  $\text{C}_{14}\text{H}_{19}\text{NO}_2$ : C, 72.07; H, 8.21; N, 6.00%.

**(2-Nitro-1-*p*-tolylethyl)cyclohexane (3in):** Obtained as pale yellow viscous oil, bp 180 °C/1 mmHg (bath temp);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  0.82–1.28 (m, 5H), 1.44–1.67 (m, 4H), 1.72–1.81 (m, 2H), 2.31 (s, 3H), 3.17–3.26 (ddd,  $J = 12.1$ , 10.1, 5.8 Hz, 1H), 4.54–4.63 (dd,  $J = 12.1$ , 10.1 Hz, 1H), 4.72–4.79 (dd,  $J = 12.1$ , 5.8 Hz, 1H), 6.99–7.03 (d,  $J = 8.0$  Hz, 2H), 7.08–7.12 (d,  $J = 8.0$  Hz, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  20.88, 25.97, 25.99, 26.03, 30.39, 30.84, 40.75, 49.76, 78.80, 127.88, 129.10, 135.58, 136.73. Found: C, 72.92; H, 8.43; N, 5.48%. Calcd for  $\text{C}_{15}\text{H}_{21}\text{NO}_2$ : C, 72.84; H, 8.56; N, 5.66%.

**3,3-Dimethyl-1-nitro-2-phenylbutane (3jm):**<sup>36</sup> Obtained as pale yellow solid (from column chromatography), white crystal (recrystallized from benzene–petroleum ether), mp 70–71 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  0.95 (s, 9H), 3.32–3.38 (dd,  $J = 5.3$ , 10.6 Hz, 1H), 4.75–4.89 (dd + dd,  $J = 5.3$ , 13.8 Hz and 10.6, 13.8 Hz, 2H), 7.16–7.19 (d,  $J = 7.3$  Hz, 2H), 7.24–7.31 (m, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  28.02, 33.68,

54.34, 77.21, 127.42, 128.13, 129.07, 137.58. Found: C, 69.38; H, 8.17; N, 6.78%. Calcd for  $\text{C}_{12}\text{H}_{17}\text{NO}_2$ : C, 69.54; H, 8.27; N, 6.76%.

**2-(2-Nitro-1-phenylethyl)thiophene (3km):** Obtained as pale yellow oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  4.80–4.95 (m, 2H), 5.05–5.11 (t,  $J = 7.9$  Hz, 1H), 6.85–6.90 (m, 2H), 7.12–7.15 (d,  $J = 5.0$  Hz, 1H), 7.20–7.44 (m, 5H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  44.46, 79.61, 124.94, 125.02, 126.86, 127.38, 127.87, 128.91, 138.63, 142.26. Found: C, 61.67; H, 4.74; N, 5.89%. Calcd for  $\text{C}_{12}\text{H}_{11}\text{NO}_2\text{S}$ : C, 61.78; H, 4.75; N, 6.00%.

**2-[2-Nitro-1-(*p*-tolyl)ethyl]thiophene (3kn):** Obtained as pale yellow oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  2.31 (s, 3H), 4.83–4.98 (dd + dd,  $J = 7.5$ , 12.6 Hz, 2H), 5.04–5.10 (t,  $J = 7.9$  Hz, 1H), 6.86–6.93 (m, 2H), 7.11–7.29 (m, 5H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  20.99, 44.29, 79.90, 124.91, 125.04, 126.92, 127.33, 129.70, 135.71, 137.77, 142.67. Found: C, 63.21; H, 5.32; N, 5.46%. Calcd for  $\text{C}_{13}\text{H}_{13}\text{NO}_2\text{S}$ : C, 63.13; H, 5.30; N, 5.66%.

**2-(2-Nitro-1-phenylethyl)furan (3lm):** Obtained as pale yellow oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  4.76–4.82 (dd,  $J = 6.9$ , 11.7 Hz, 1H), 4.89–4.94 (t,  $J = 7.3$  Hz, 1H), 4.97–5.04 (dd,  $J = 7.6$ , 11.7 Hz, 1H), 6.10–6.12 (d,  $J = 3.0$  Hz, 1H), 6.29–6.32 (dd,  $J = 1.8$ , 2.9 Hz, 1H), 7.23–7.36 (m, 6H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  43.49, 78.01, 107.40, 110.42, 127.83, 128.07, 129.03, 136.87, 142.52, 151.98. Found: C, 66.21; H, 5.10; N, 6.15%. Calcd for  $\text{C}_{12}\text{H}_{11}\text{NO}_3$ : C, 66.35; H, 5.10; N, 6.45%.

**2-[2-Nitro-1-(*p*-tolyl)ethyl]furan (3ln):** Obtained as pale yellow oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  2.31 (s, 3H), 4.72–4.79 (dd,  $J = 7.4$ , 11.1 Hz, 1H), 4.84–4.90 (t,  $J = 7.4$  Hz, 1H), 4.94–5.01 (dd,  $J = 7.4$ , 11.1 Hz, 1H), 6.08–6.10 (d,  $J = 1.8$  Hz, 1H), 6.27–6.30 (t,  $J = 1.8$  Hz, 1H), 7.11–7.17 (m, 4H), 7.33–7.35 (d,  $J = 1.8$  Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  20.99, 43.11, 78.06, 107.21, 110.35, 127.65, 129.64, 133.79, 137.80, 142.41, 152.20. Found: C, 67.24; H, 5.77; N, 5.57%. Calcd for  $\text{C}_{13}\text{H}_{13}\text{NO}_3$ : C, 67.52; H, 5.67; N, 6.06%.

The following three new compounds and a known **3dn**,<sup>35</sup> which appeared in Scheme 1, but not in the Tables, were isolated. Their physical data are also shown here.

**1-(*p*-Methoxyphenyl)-2-nitro-1-(*p*-tolyl)ethane (3cn):** Obtained as yellow oil; 55% isolated yield;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  2.29 (s, 3H), 3.72 (s, 3H), 4.80–4.90 (m, 3H), 6.82–6.85 (d,  $J = 8.1$  Hz, 2H), 7.08–7.16 (m, 6H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  20.87, 47.83, 55.08, 79.39, 114.24, 127.36, 127.60, 129.56, 131.46, 136.59, 137.02, 158.77. Found: C, 70.78; H, 6.16; N, 4.88%. Calcd for  $\text{C}_{16}\text{H}_{17}\text{NO}_3$ : C, 70.83; H, 6.32; N, 5.16%.

**1-(*p*-Chlorophenyl)-2-nitro-1-(*p*-tolyl)ethane (3dn):** Obtained as pale yellow oil (lit. bp 174 °C/0.5 mmHg<sup>35</sup>); 63% isolated yield;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  2.26 (s, 3H), 4.79–4.88 (m, 3H), 7.07–7.14 (m, 6H), 7.21–7.24 (d,  $J = 7.0$  Hz, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  20.76, 47.75, 78.76, 127.22, 128.82, 128.89, 129.60, 133.07, 135.59, 137.28, 137.92.

**2-Nitro-1-(*m*-nitrophenyl)-1-(*p*-tolyl)ethane (3fn):** Obtained as pale yellow viscous oil; 62% isolated yield;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  2.31 (s, 3H), 4.94–5.10 (m, 3H), 7.10–7.13 (d,  $J = 8.2$  Hz, 2H), 7.14–7.18 (d,  $J = 8.2$  Hz, 2H), 7.46–7.52 (t,  $J = 7.8$  Hz, 1H), 7.61–7.65 (d,  $J = 9.2$  Hz, 1H), 8.07–8.13 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  20.90, 48.10, 78.54, 122.50, 127.33, 129.96, 133.76, 134.72, 137.96, 141.62, 148.48. Found: C, 63.00; H, 4.96; N, 9.76%. Calcd for  $\text{C}_{15}\text{H}_{14}\text{N}_2\text{O}_4$ : C, 62.93; H, 4.93; N, 9.79%.

**2-Nitro-1-(*o*-nitrophenyl)-1-(*p*-tolyl)ethane (3gn):** Obtained as pale yellow viscous oil; 52% isolated yield;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  2.28 (s, 3H), 4.92–5.11 (dd + dd,  $J = 8.0$ , 13.8 Hz, 2H), 5.55–5.62 (t,  $J = 8.0$  Hz, 1H), 7.08–7.14 (m, 4H), 7.36–7.43 (m, 2H), 7.52–7.59 (t,  $J = 7.7$  Hz, 1H), 7.83–7.87 (d,  $J = 8.1$  Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  20.98, 42.73, 78.01, 125.27, 127.67, 128.52, 129.10, 129.82, 133.24, 133.75, 134.34, 137.82, 149.49. Found: C, 62.51; H, 4.93; N, 9.71%. Calcd for  $\text{C}_{15}\text{H}_{14}\text{N}_2\text{O}_4$ : C, 62.93; H, 4.93; N, 9.79%.

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