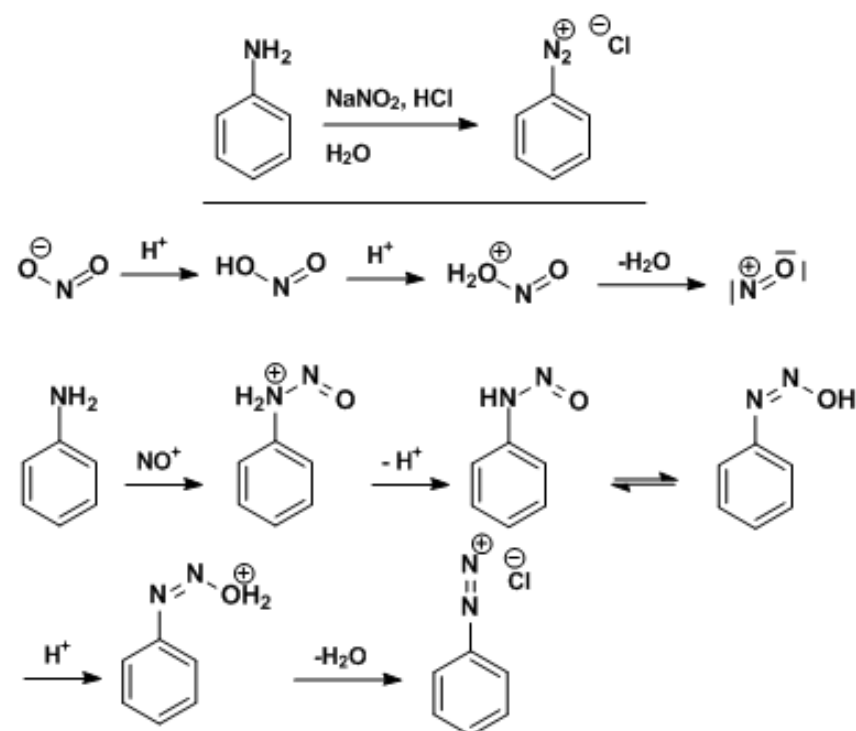
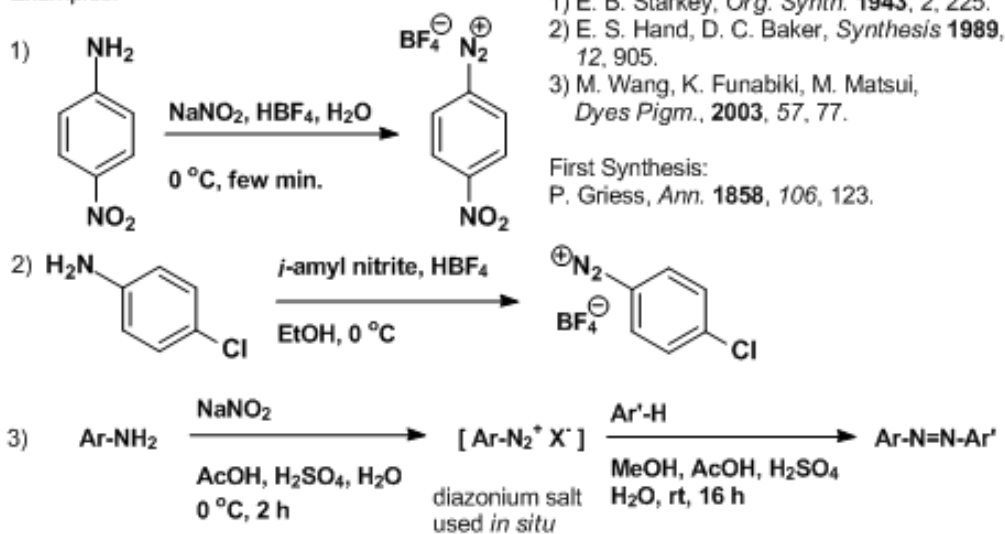


## I. Diazotation, Diazonation, or Diazotization



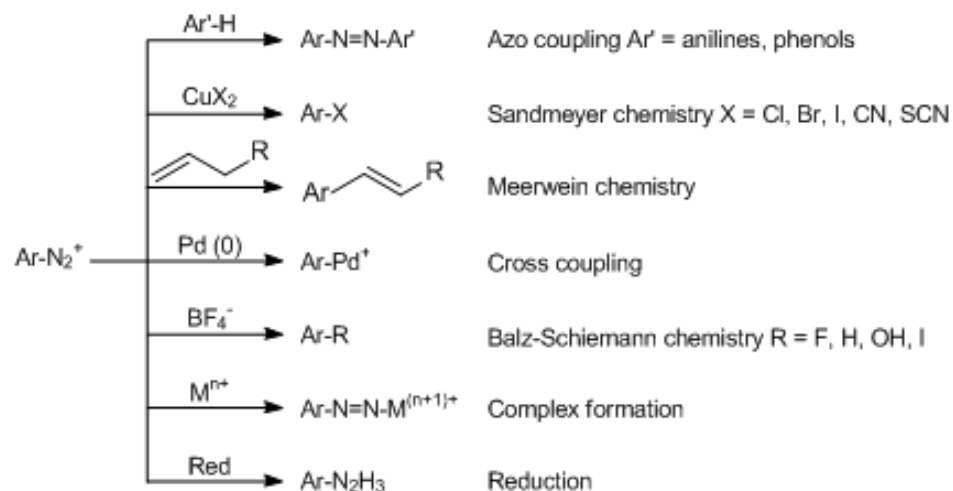
Examples:



- 1) E. B. Starkey, *Org. Synth.* **1943**, 2, 225.
- 2) E. S. Hand, D. C. Baker, *Synthesis* **1989**, 12, 905.
- 3) M. Wang, K. Funabiki, M. Matsui, *Dyes Pigm.*, **2003**, 57, 77.

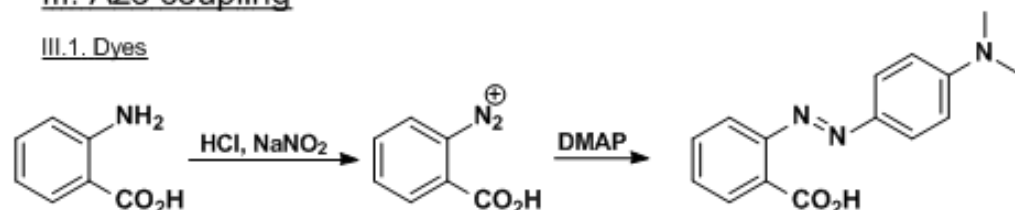
First Synthesis:  
P. Griess, *Ann.* **1858**, 106, 123.

## II. Summary of reaction pathways



## III. Azo coupling

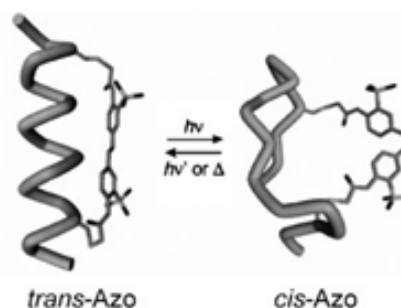
## III.1. Dyes



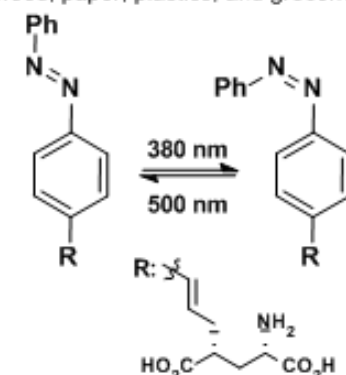
Methyl Red

60-70 % of all dyes are azo dyes. Bright, intense colors; mainly yellow, orange, red, but also blue is available. They are used to dye textiles, fats, oils, wax, wood, paper, plastics, and groceries.

## III.2. Photo switches



J.-C. Micheau, J. Zhao, *J. Phys. Org. Chem.* **2007**, 20, 810.



M. Volgraf, P. Gorostiza, S. Szobota, M. R. Helix, E. Y. Isacoff, D. Trauner, *JACS* **2007**, 129, 260.

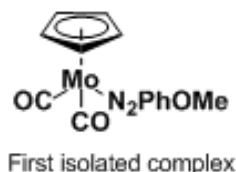
## IV. Complex formation

$\text{ArN}_2^+$  is isoelectronic with  $\text{CO}$ ,  $\text{NO}^+$ , and  $\text{RNC}$ .  
Numerous  $\text{ArN}_2^+$  - transition metal complexes have been isolated.

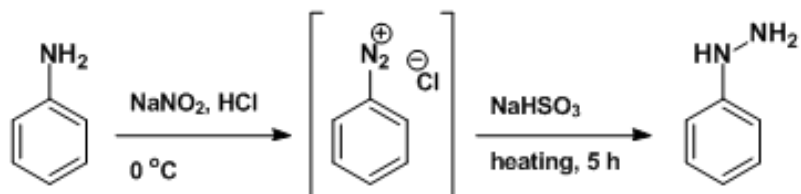
Reviews:

R. B. King, *J. Organomet. Chem.* **1995**, 187.

D. Sutton, *Chem. Rev.* **1993**, 93, 995.



## V. Reduction



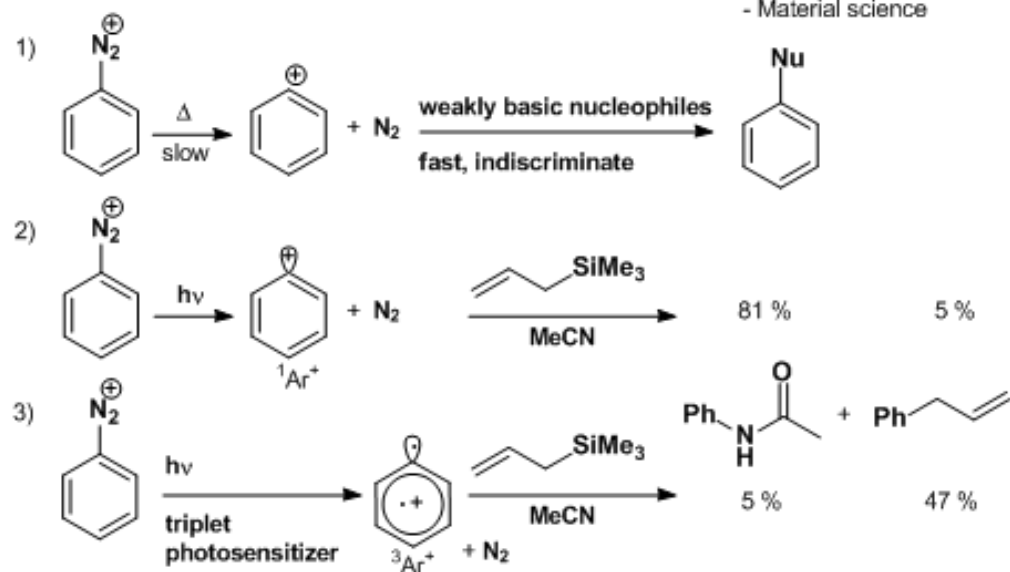
J. R. Robinson, N. E. Good, *Can. J. Chem.* **1957**, 35, 1578.

One example of many, SciFinder yielded 458 papers for this reaction.

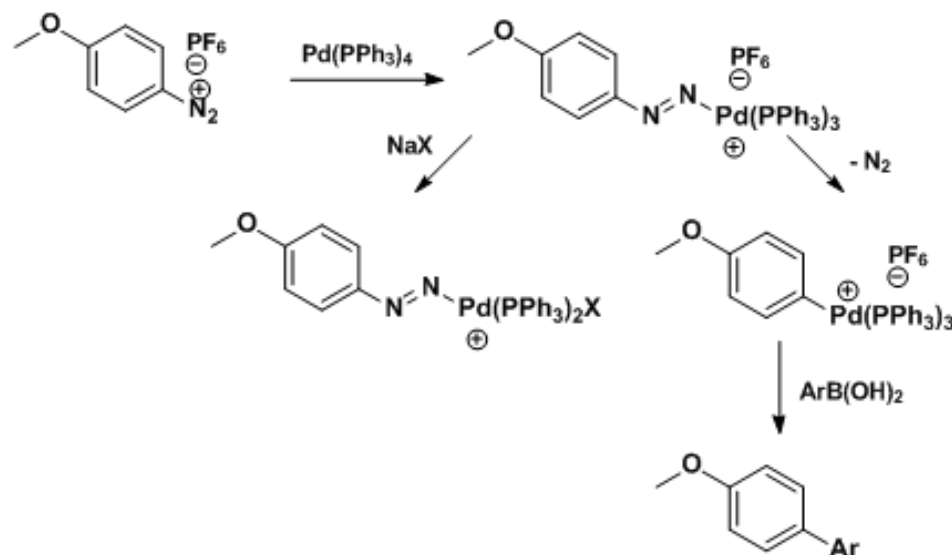
## VI. Dediazonation

## VI.1. Heterolytic C-N bond cleavage

Examples: - Balz-Schiemann Reaction  
Kuerti, Czako, page 34  
- Material science

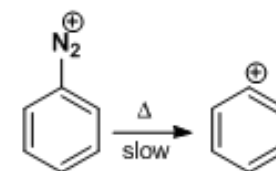
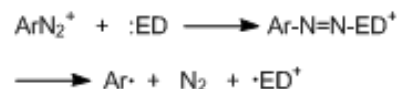
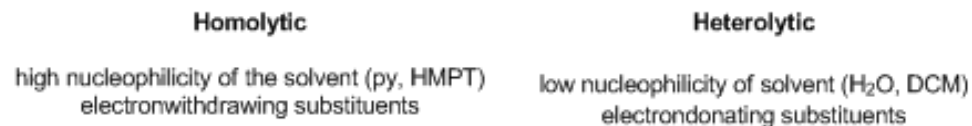


## Dediazonation by palladium



R. Yamashita, K. Kikukawa, F. Wada, T. Matsuda, *J. Organomet. Chem.* **1980**, 201, 463.

## VI.2. Mixed processes - Solvolysis



in acidic methanol: under  $\text{O}_2$  exclusion

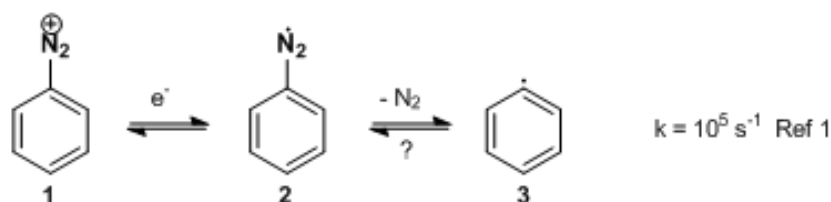
when  $\text{O}_2$  is present

I. Szele, H. Zollinger, *Helv. Chim. Acta* **1978**, 61, 1721.

D. F. DeTar, M. N. Turetzky, *JACS* **1955**, 77, 1745.

## VI.3. Homolytic Dediazonation

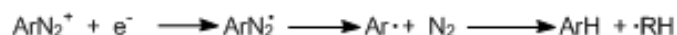
## General considerations



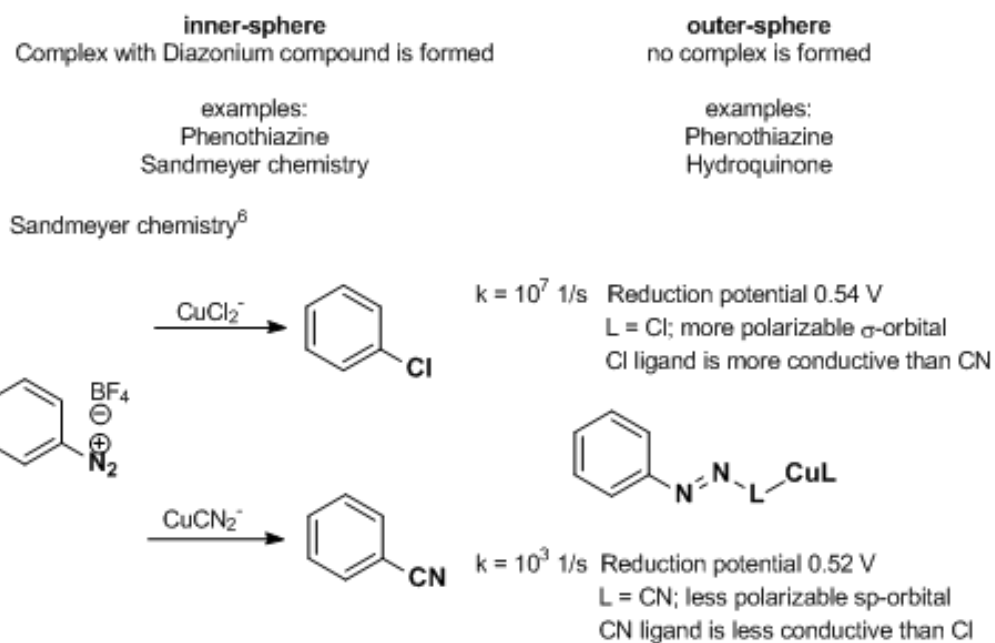
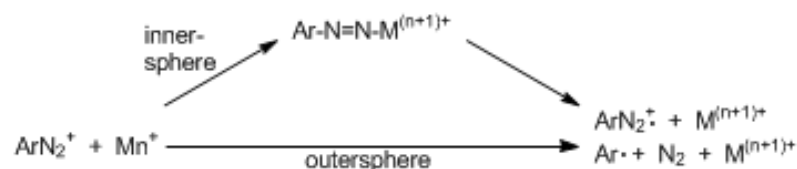
Experimental evidence for electrontransfer:

- Electrochemical:<sup>2</sup> electronwithdrawing substituents facilitate reduction - stabilize **2**.  
electron donating substituents impede reduction - stabilize **1**.
- Photoinduction:<sup>3</sup> rate of electrontransfer from pyrene to  $\text{ArN}_2^+$  was measured.
- Pulse radiolysis: -  $\text{Ar-N=N-N=N-Ar}$  was detected.<sup>4</sup>  
- Alcohols sustain a radical-chain mechanism of reduction.<sup>5</sup>

Electrontransfer:

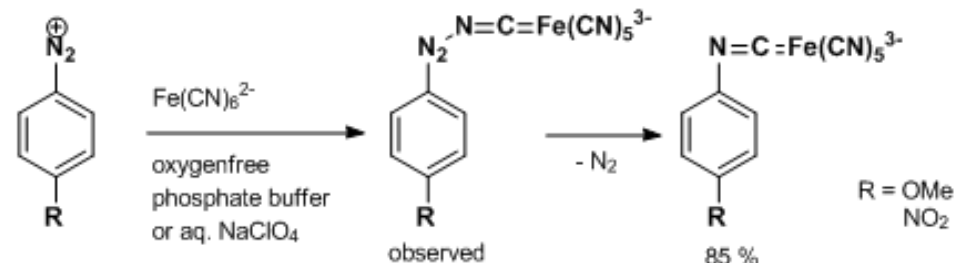
Dediazonation by metal ions<sup>1</sup>

Electrontransfer from metal ions to aryldiazonium salts has been shown with Sn(II), Cr(II), Ti(III), V(II), Fe(II), and Cu(I). Cu is superior to all other tested metals as it has the ideal redox potential.



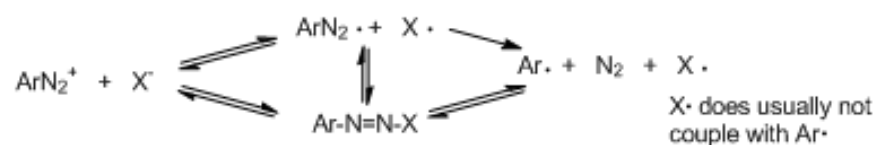
Inner sphere mechanism is currently favoured, but an outer-sphere mechanism is not ruled out.

Still ongoing discussion

 $\text{Fe}(\text{CN})_6^{4-}$  was believed to react via an outer-sphere mechanism,<sup>7</sup> but:<sup>8</sup>

In oxygen-containing solutions phenol is obtained.

<sup>1</sup> Summary in C. Galli, *Chem. Rev.* **1988**, 88, 765 (p. 769f for kinetics and p. 771f for metal cat.).<sup>2</sup> R. M. Eloffson, F. F. Gadallah, *J. Org. Chem.* **1969**, 34, 854.<sup>3</sup> H. G. O. Becker, R. Ebisch, G. Israel, G. Kroha, W. Kroha, O. Brede, R. Mehnert, *J. Prakt. Chem.* **1977**, 319, 98.<sup>4</sup> O. Brede, R. Mehnert, W. Naumann, H. G. O. Becker, *Radiochem. Radioanal. Lett.* **1979**, 39, 247.<sup>5</sup> E. S. Lewis, D. J. Chambers, *JACS* **1971**, 93, 3267.<sup>6</sup> P. Hanson, S. C. Rowell, J. R. Jones, P. H. Walton, A. W. Timms, *J. Chem. Soc., Perkin Trans. 2* **2002**, 1126.<sup>7</sup> M. P. Doyle, J. K. Guy, K. C. Brown, S. N. Mahapatro, C. M. VanZyl, J. R. Pladziewicz, *JACS* **1987**, 109, 1536.<sup>8</sup> U. Klaening, T. Lund, H. Lund, S. U. Pedersen, K. Daasbjerg, *J. Phys. Chem. A* **2010**, 114, 6575.

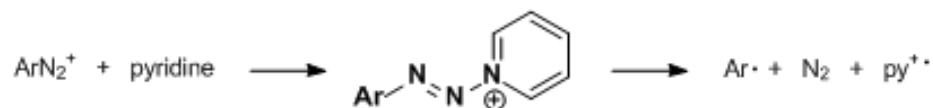
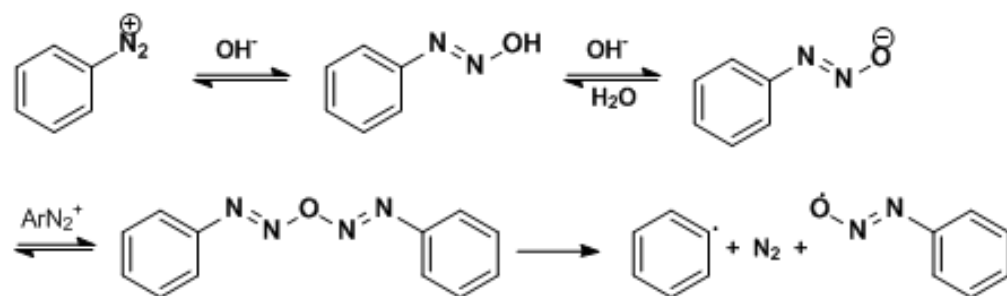
Dediazonation by anions<sup>9</sup>

**inner-sphere**  
low dielectric constant of solvent

examples:  
ArS<sup>-</sup>, OH<sup>-</sup>, RO<sup>-</sup>, pyridine

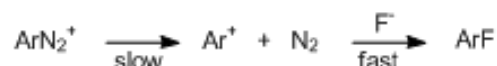
**outer-sphere**  
suitable redox potential

examples:  
I<sup>-</sup>, Br<sup>-</sup>, ArS<sup>-</sup>, Xanthate, Amines, H<sub>2</sub>PO<sub>3</sub><sup>-</sup>

Gomberg-Bachmann Reaction<sup>10</sup>

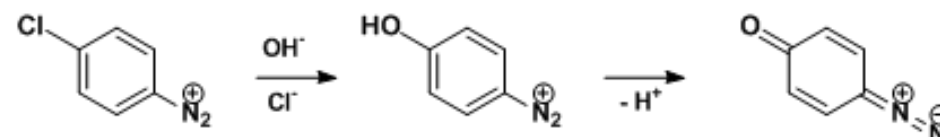
## Fluorine

Anions, which are not good electron donors can lead to a heterolytic pathway.

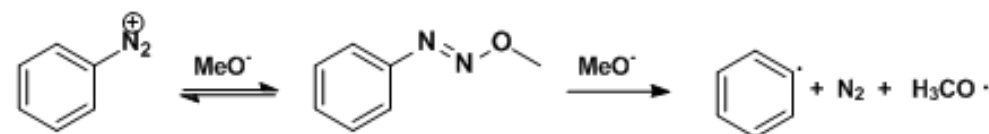


<sup>9</sup> Summary in C. Galli, *Chem. Rev.* **1988**, 88, 765 (p. 773f).

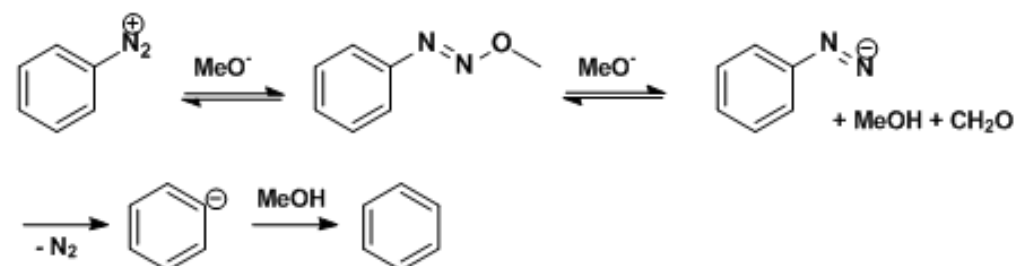
<sup>10</sup> M. Gomberg, W. E. Bachmann, *JACS* **1924**, 46, 2339.

Nucleophilic aromatic substitution<sup>11</sup>Methanolate<sup>12</sup>

basic conditions



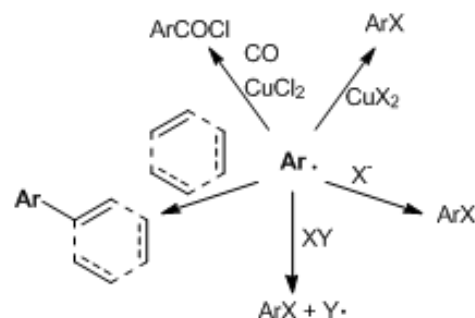
strongly basic conditions (heterolytic)



<sup>11</sup> J. Besse, W. Schwarz, H. Zollinger, *Helv. Chim. Acta* **1981**, 64, 504.

<sup>12</sup> T. J. Broxton, J. F. Bunnett, C. H. Paik, *J. Org. Chem.* **1977**, 42, 643.

## VII. Reactions of the Arylradical



Cu-catalyzed Sandmeyer chemistry

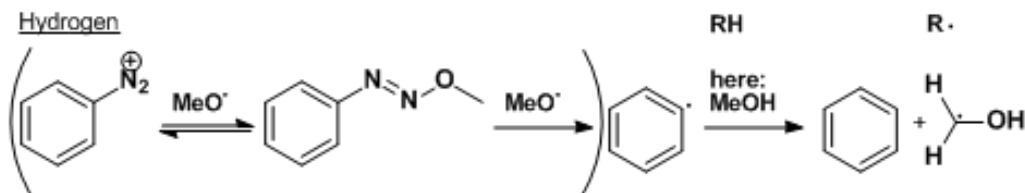
Coupling with a nucleophile

Atom transfer

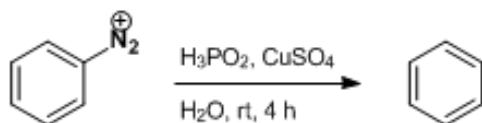
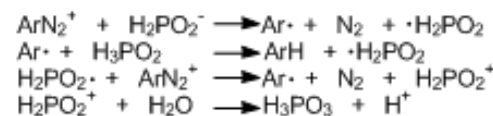
Addition to a  $\pi$ -systemCoupling with CO/SO<sub>2</sub>

## VII.1. Atom transfer

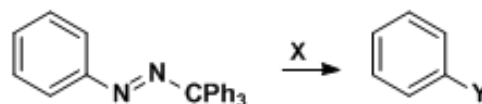
## Hydrogen



Often the main product as a hydrogen atom can be transferred from the solvent.

 $k = 10^5$  to  $10^6$  1/sHydro-dediazoniating is best performed with hypophosphorous acid under Cu-catalysis.<sup>13</sup>

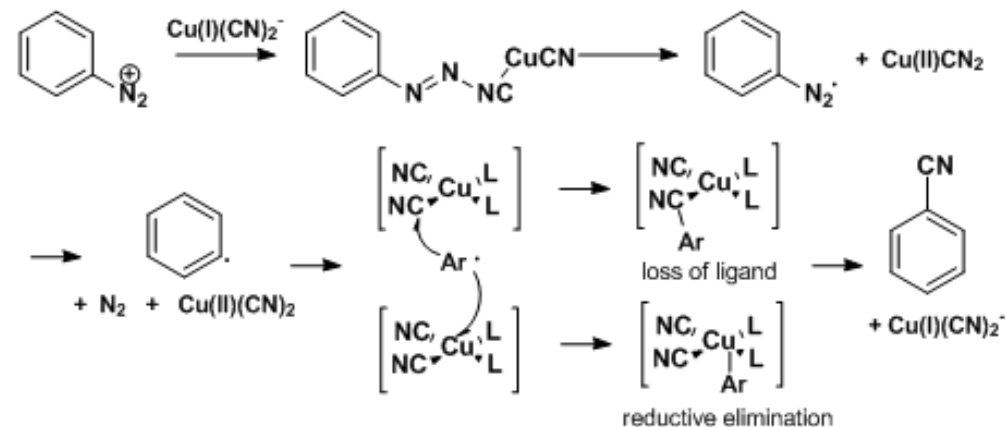
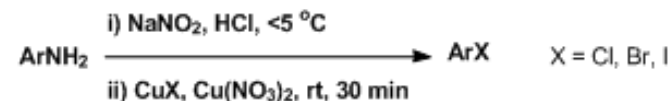
## Halogens

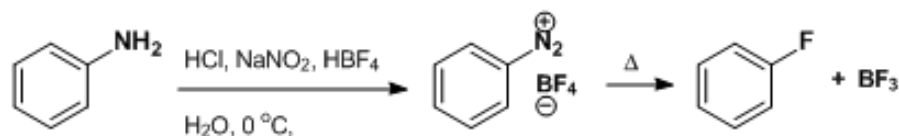


X <sup>14</sup>	k	Y
MeOH	5x10 <sup>5</sup>	H
tert-alkyl	2x10 <sup>6</sup>	H
I <sub>2</sub>	1x10 <sup>10</sup>	I
ArI	9x10 <sup>7</sup>	I
CBr <sub>4</sub>	5x10 <sup>9</sup>	Br
PhH	1x10 <sup>6</sup>	Ph
Ethylen	8x10 <sup>6</sup>	CH <sub>2</sub> CH <sub>3</sub>

<sup>13</sup> N. Kornblum, G. D. Cooper, J. E. Taylor, *JACS* **1950**, 72, 3013.<sup>14</sup> R. G. Kryger, J. P. Lorand, N. R. Stevens, N. R. Herron, *JACS* **1977**, 99, 7589.

## VII.2. Cu-catalyzed Sandmeyer chemistry

T. Sandmeyer, *Chem. Ber.* **1884**, 17, 1633, 2650 (original procedure):C. Galli, *J. Chem. Soc. Perkin Trans. 2* **1981**, 1459:The reaction can be improved by addition of poly(ethylene glycols)<sup>15</sup> or crown ethers.<sup>16</sup>Nucleophiles used in Sandmeyer chemistry: Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, CN<sup>-</sup>, NO<sub>2</sub><sup>-</sup>, OH<sup>-</sup>Nucleophiles not used: SO<sub>4</sub><sup>2-</sup>, ClO<sub>4</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>T. Cohen, A. G. Dietz, J. R. Miser, *J. Org. Chem.* **1977**, 42, 2053.P. Hanson, S. C. Rowell, J. R. Jones, P. H. Walton, A. W. Timms, *J. Chem. Soc., Perkin Trans. 2* **2002**, 1126 (Mechanism).<sup>15</sup> N. Suzuki, Y. Kaneko, T. Nomoto, Y. Izawa, *Chem. Comm.* **1984**, 1523.<sup>16</sup> R. A. Bartach, H. Chen, N. F. Haddock, P. N. Juri, *JACS* **1976**, 98, 6753.

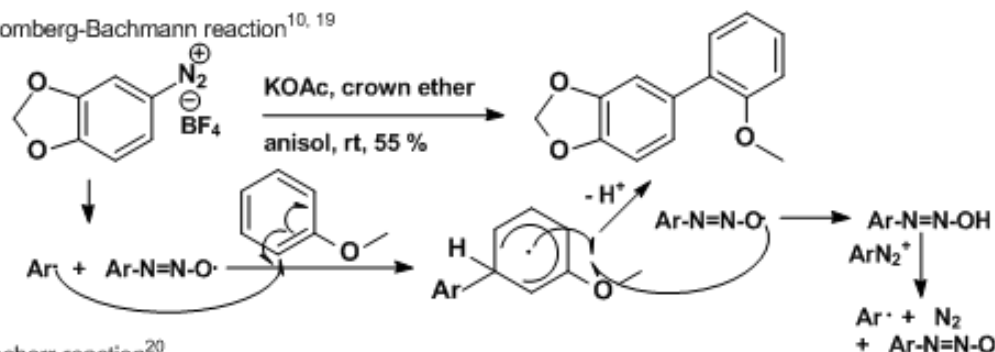
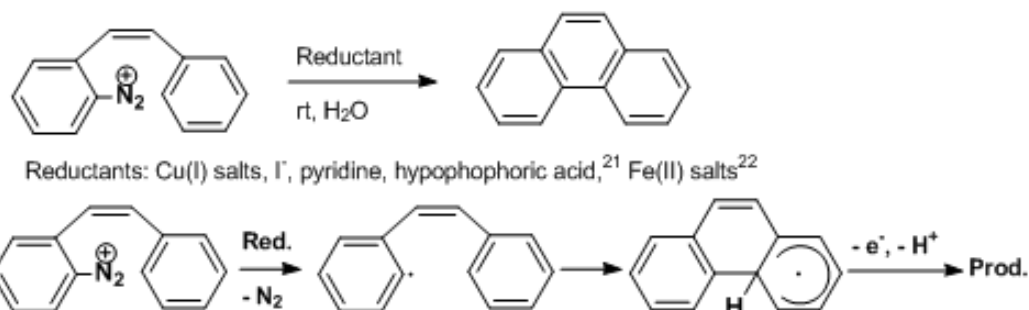
Insertion: Balz-Schiemann Reaction<sup>17</sup>

Sandmeyer conditions will not yield fluorinated aryls due to the high oxidation potential of F and the inefficiency of the transfer of the fluoride ligand from the copper salt.

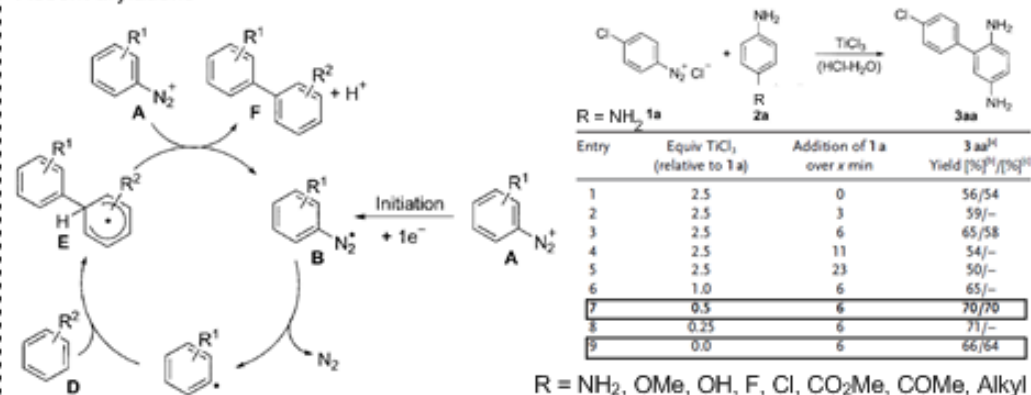
In absence of  $\text{BF}_4^-$  phenols can be prepared.

Other arylhalogenides are available by this procedure, but Sandmeyer conditions are superior.<sup>18</sup>

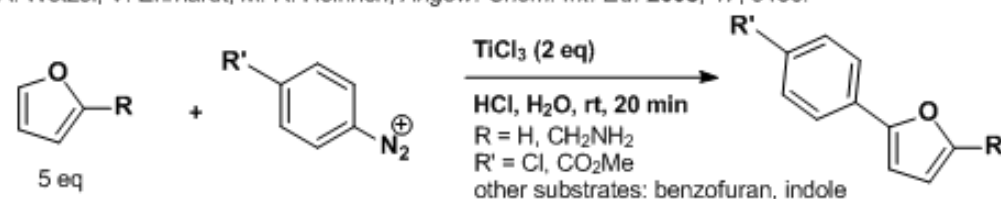
## VII.3. Addition to aromatic systems

Gomberg-Bachmann reaction<sup>10, 19</sup>Pschorr reaction<sup>20</sup>

## Recent arylations

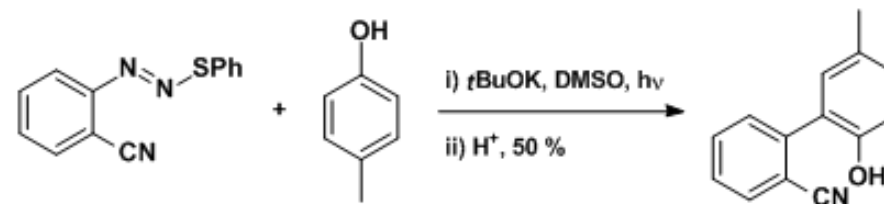


A. Wetzel, V. Ehrhardt, M. R. Heinrich, *Angew. Chem. Int. Ed.* **2008**, *47*, 9130.

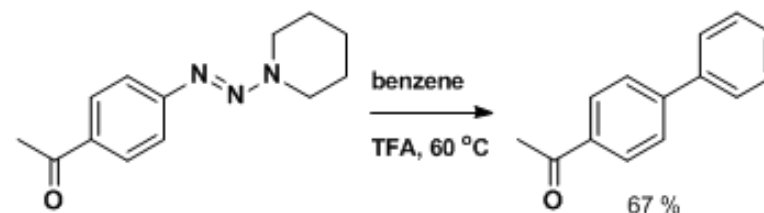


A. Wetzel, G. Pratsch, R. Kolb, M. R. Heinrich, *Chem. Eur. J.* **2010**, *16*, 2547.

Electronrich arens are suitable substrates, but these tend to undergo diazocoupling. Thus the diazonium salt has to be added slowly (see above) or "protected" (see below).



G. Petrillo, M. Novi, C. Dell'Erba, C. Tavani, *Tetrahedron* **1991**, *47*, 9297.



Synthesis of Biaryls from Aryltriazenes, *J. Org. Chem.* **1985**, *50*, 2232.

<sup>17</sup> D. T. Flood, *Org. Synth. Coll. Vol.* **2** **1943**, 295; R. A. Abramovitch, J. G. Saha, *Can. J. Chem.* **1965**, *43*, 3269.

<sup>18</sup> G. A. Ohla, W. S. Tolgyesi, *J. Org. Chem.* **1961**, *26*, 2053.

<sup>19</sup> J. J. Li, *Name Reactions*, Springer (Berlin) **2009**, 262.

<sup>20</sup> R. Pschorr, *Chem. Ber.* **1896**, *29*, 496.

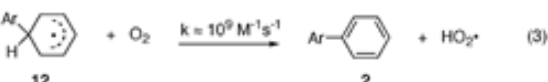
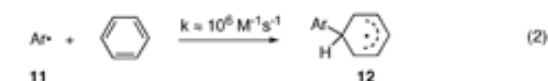
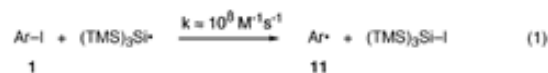
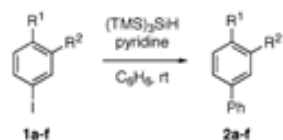
<sup>21</sup> C. Galli, *Chem. Rev.* **1988**, *88*, 765 (p. 781).

<sup>22</sup> F. W. Wassmundt, W. F. Kiesman, *J. Org. Chem.* **1995**, *60*, 196.

## Some informative examples not based on aryldiazonium salts

In modern variations aryl radicals are generated from aryl hydrazines,<sup>23</sup> and grignard reagents,<sup>24</sup> or from halides using organotin, organosilicon, or samarium compounds.<sup>25</sup> And Carboxylic and boronic acids.<sup>26</sup>

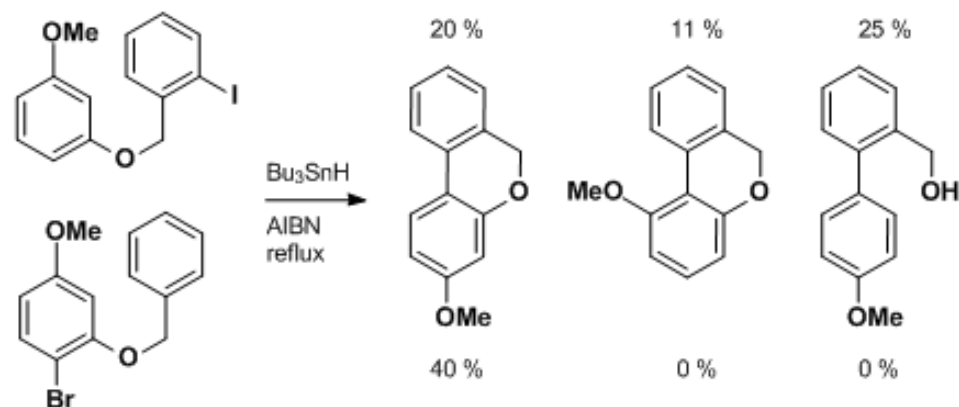
- Oxidation of the coupling product performed by oxygen<sup>27</sup>



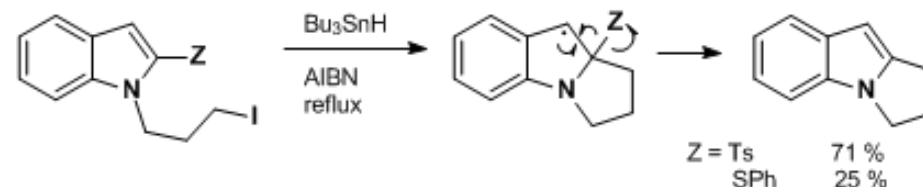
entry	aryl iodide	R <sup>1</sup>	R <sup>2</sup>	product	% yield <sup>b</sup>
1	1a	CO <sub>2</sub> Me	H	2a	87
2	1b	H	H	2b	75
3	1c	OMe	H	2c	90
4	1d	H	CO <sub>2</sub> Et	2d	82
5	1e	t-Bu	H	2e	90
6	1f	H	OMe	2f	89

<sup>a</sup>rxn conds: 1, (TMS)<sub>3</sub>SiH (1.2 equiv), and pyridine (5 equiv) were dissolved in benzene (50 mL, 4 mM). <sup>b</sup>isolated yields

- 5-ring formation (5-exo) preferred to 6-ring formation (6-endo).

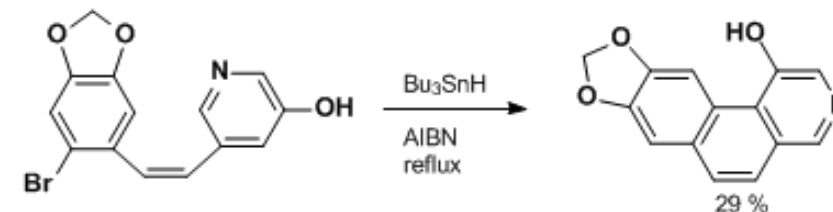


- Radical leaving group leads to ipso substitution.
- Tosyl substituents are specially good leaving groups.



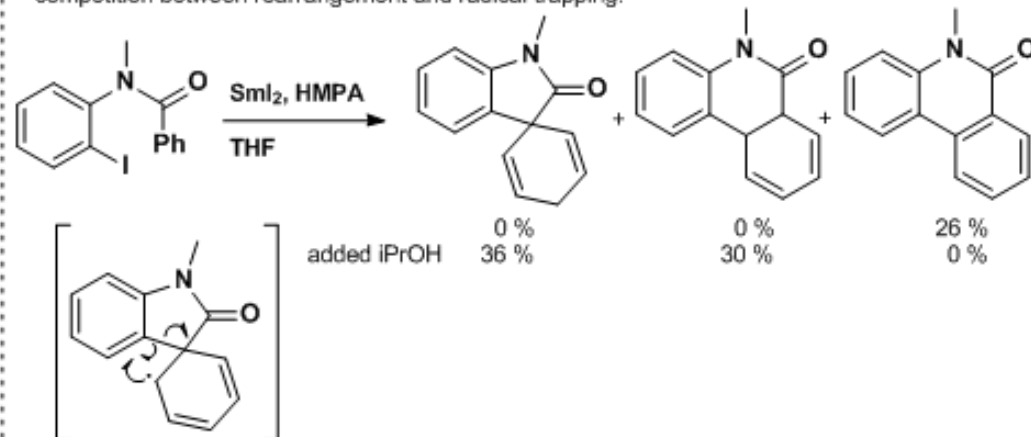
S. Caddick, K. Abutayab, K. Jenkins, R. I. West, *J. Chem. Soc. Perkin Trans. 1* **1996**, 675.

- Synthesis of heterocycles (Todaquinoline).



D. C. Harrowen, M. I. T. Nunn, N. J. Blumire, D. R. Fenwick, *Tet. Lett.* **2000**, 6681.

- breaking of aromaticity possible.
- competition between rearrangement and radical trapping.



H. Ohno, H. Iwasaka, T. Eguchi, T. Tanaka, *Chem. Comm.* **2004**, 2228.

<sup>23</sup> A. S. Demir, O. Reis, E. Oezguel-Karaaslan, *J. Chem. Soc. Perkin Trans. 1* **2001**, 3042.

<sup>25</sup> W. R. Bowman, J. M. D. Storey, *Chem. Soc. Rev.* **2007**, 36, 1803; D. P. Curran, A. I. Keller, *JACS* **2006**, 128, 13706.

<sup>26</sup> I. B. Seiple, S. Su, R. A. Rodriguez, R. Gianatassio, Y. Fujiwara, A. L. Sobel, P. S. Baran, *JACS* **2010**, 132, 13194.

<sup>27</sup> W. R. Bowman, E. Mann, J. Parr, *J. Chem. Soc. Perkin Trans. 1* **2000**, 2991.

## VII.3. Addition to olefins

## Meerwein reaction



$R_1 = \text{H, alkyl, O-alkyl, Cl, Br, I, CO}_2\text{-alkyl, CONHR, SO}_2\text{R, NO}_2, \text{CF}_3$

$R_2 = \text{H, alkyl, aryl, CHO, CO-alkyl, CO}_2\text{-alkyl, CO}_2\text{H, CO}_2\text{NH}_2, \text{CO}_2\text{NR}_2, \text{CN, alkenyl, Cl, Br}$

$X = \text{Cl, Br}$

$Y = \text{H, ArN}_2^+, \text{OR, SR, Cl, Br, I, CN}$

solvent: acetone, MeCN

Three classes of Meerwein arylation substrates:

- 1) Activated olefins - acceptor-substituted or conjugated olefins
- 2) Non-activated olefins - only  $\text{sp}^3$ -carbons adjacent to double bond
- 3) Borderline cases - e.g. vinyl ethers, vinyl halogenides, vinyl trifluoromethanes

## Activated olefins

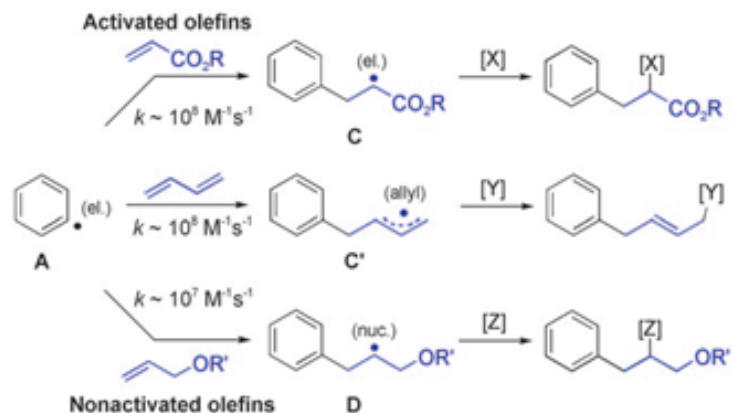
usual substrates

fast addition to the aryl radical  
can undergo polymerisations  
form electrophilic radical  
use nucleophilic trapping agent  
(Sandmeyer product formation possible)

## Non-activated olefins

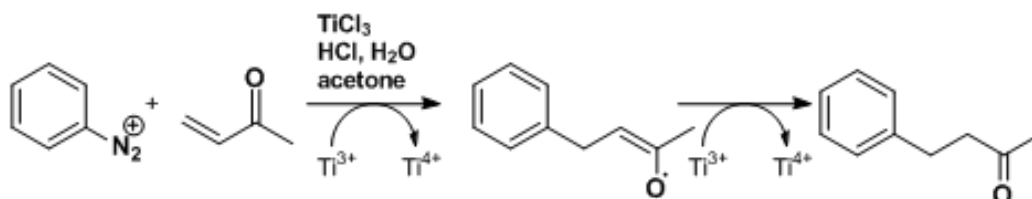
relatively slow addition to aryl radical  
do not polymerise

form nucleophilic radical  
use electrophilic trapping agent  
(Sandmeyer product formation unlikely)



M. R. Heinrich, *Chem. Eur. J.* **2009**, *15*, 820.

## Trapping by Hydrogen - Ti(III)-catalyzed Meerwein reaction

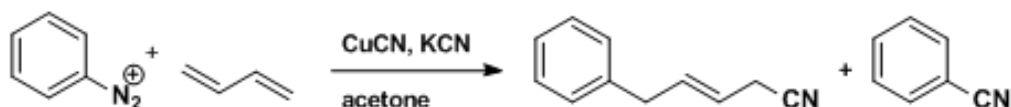


further substrates: maleinic and fumaric acids, vinyl sulfones, vinyl phosphonates, acrylonitrile  
unactivated olefins give yields < 10 %

A. Citterio et al. *Synthesis* **1980**, 291; *Synthesis* **1986**, 308.

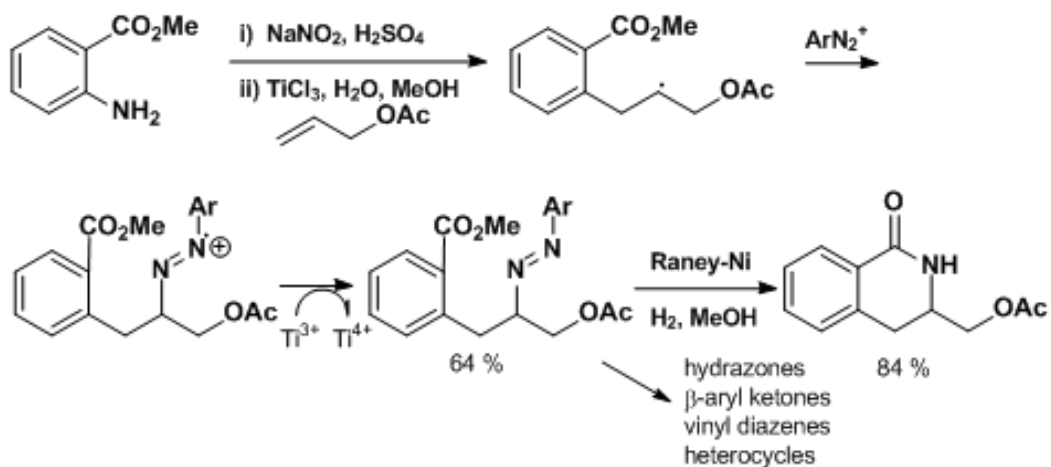
H. I. Tashtoush, R. Sustmann, *Chem. Ber.* **1993**, *126*, 1759.

## Trapping by CN - Carbocyanation



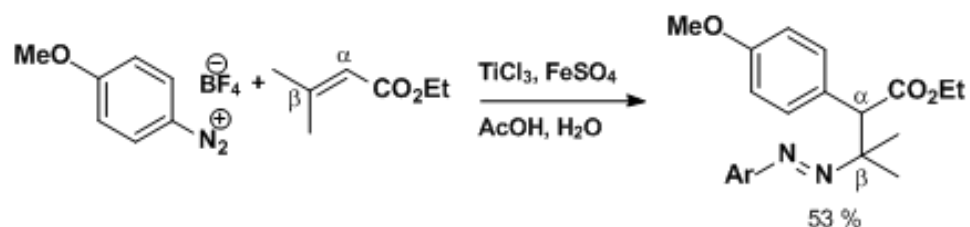
N. D. Obushak, N. I. Ganushchak, V. S. Matiichuk, *Russ. J. Org. Chem.* **1996**, *32*, 766.

## Trapping with Aryldiazonium ion - Carboamination



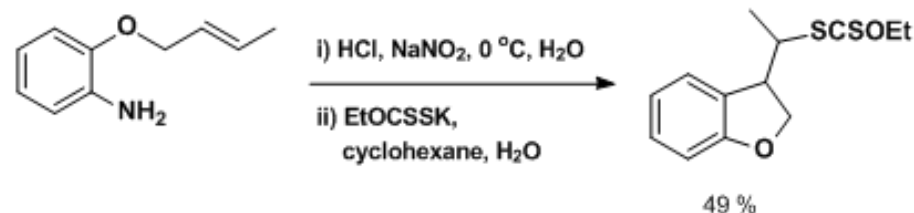
M. R. Heinrich, O. Blank, S. Woelfel, *Org. Lett.* **2006**, *8*, 3323.





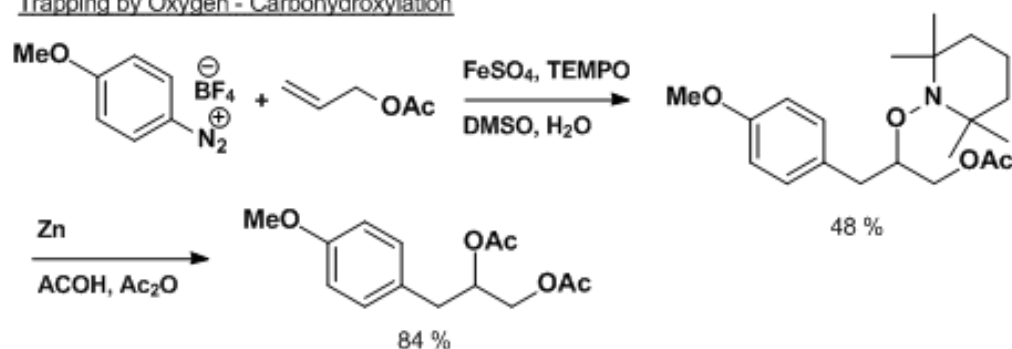
Sterically hindered  $\beta$ -position induces attack of the radical in the  $\alpha$ -position.

A. Citterio, F. Minisci, A. Albinati, S. Bruckner, *Tet. Lett.* **1980**, 2909.

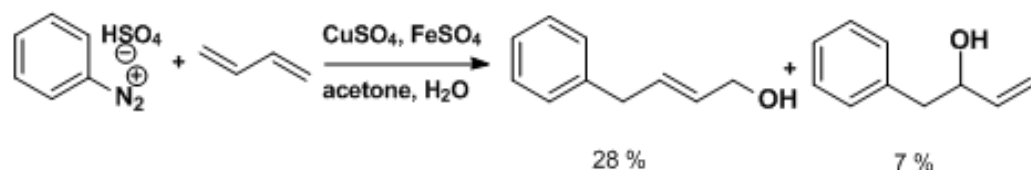


L. Tournier, Z. Zard, *Tet. Lett.* **2005**, 46, 971.

#### Trapping by Oxygen - Carbohydroxylation

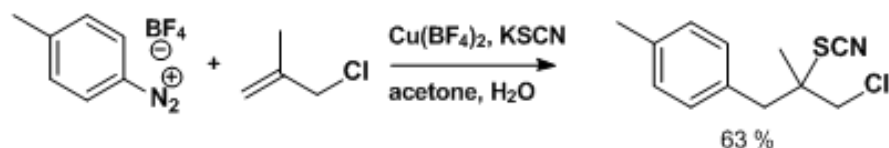


M. R. Heinrich, A. Wetzel, M. Kirschstein, *Org. Lett.* **2007**, 9, 3833.



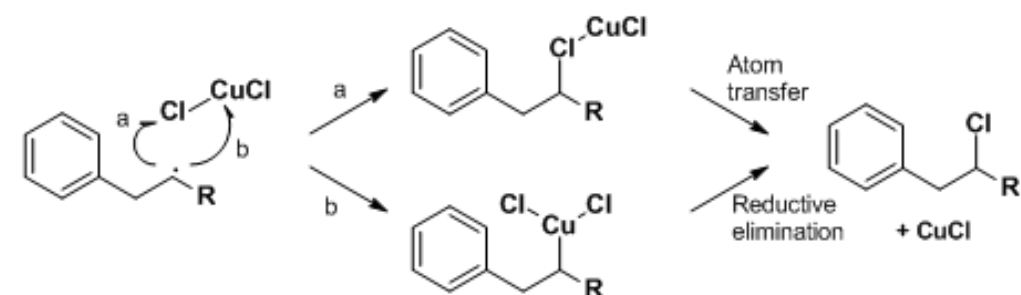
M. R. Heinrich, *Chem. Eur. J.* **2009**, 15, 820; N. I. Ganushchak, B. D. Grishchuk, A. V. Dombrovskii, *Zh. Org. Khim.* **1973**, 9, 1030 (paper cited in Heinrich review).

#### Trapping by Sulfur - Carbothionylation



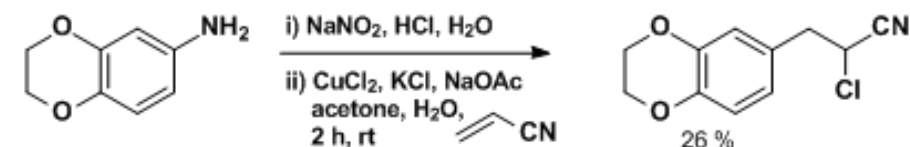
M. R. Heinrich, *Chem. Eur. J.* **2009**, 15, 820; P. M. Gorbovoi, G. N. Tulaidan, B. D. Grishchuk, *Russ. J. Gen. Chem.* **2008**, 78, 133 (paper cited in Heinrich review).

#### Trapping by Chlorine - Carbochlorination



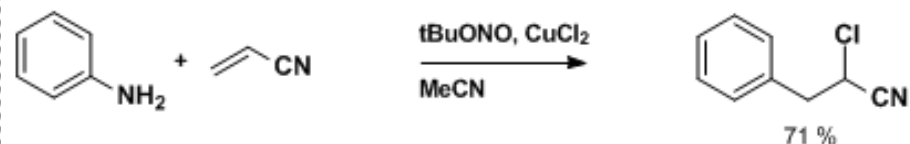
H. Brunner, C. Buechel, M. P. Doyle, *J. Organomet. Chem.* **1997**, 541, 89.

#### Standard Meerwein conditions



G. J. Wells, M. Tao, K. A. Josef, R. Bihovsky, *J. Med. Chem.* **2001**, 44, 3488.

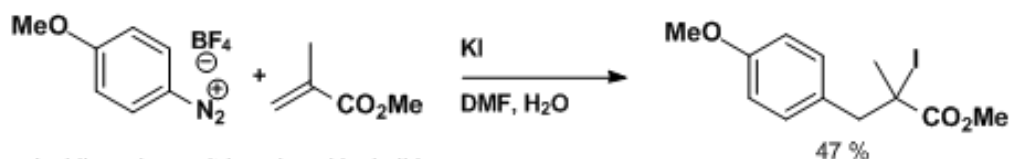
#### Alternative Meerwein conditions



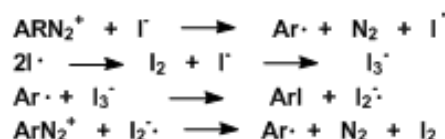
M. P. Doyle, B. Siegfried, R. C. Elliot, J. F. Dellaria Jr, *J. Org. Chem.* **1977**, 42, 2431.

Trapping by Bromine - Carbobromination

Achieved under almost identical conditions as for chlorine. Lower yields are observed, because of a higher tendency to form Sandmeyer products.

Trapping by Iodine - Carboiodination

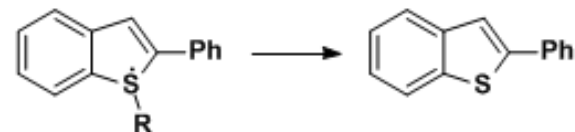
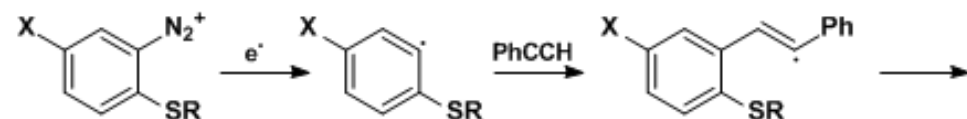
Aryldiazonium salt is reduced by iodide.



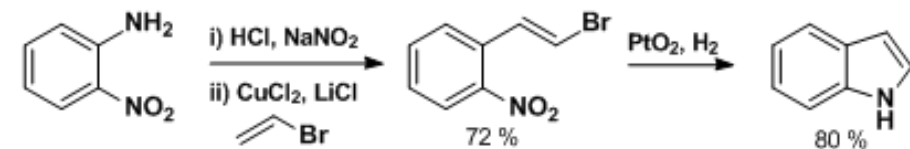
C. Galli, *Chem. Rev.* **1988**, 88, 765  
M. R. Heinrich, *Chem. Eur. J.* **2009**, 15, 820.

Related reactions

J. K. Kochi, *Tetrahedron* **1962**, 18, 483.



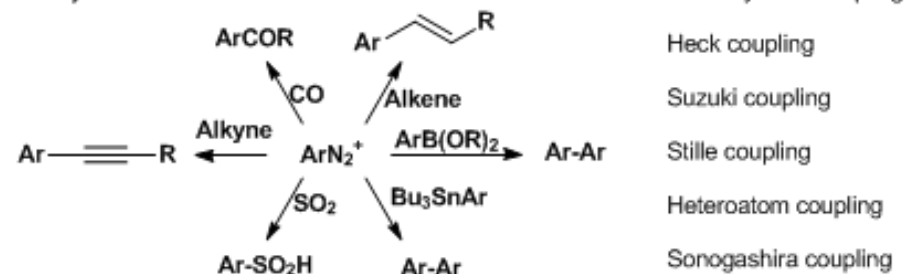
R. Leardini, G. F. Pedulli, A. Tundo, G. Zanardi, *Chem. Comm.* **1985**, 1390.



S. Raucher, G. A. Koolpe, *J. Org. Chem.* **1983**, 2066.

VIII. Pd-catalyzed cross-coupling

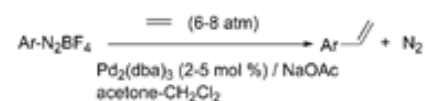
Summary:



Review: A. Roglans, A. Pla-Quintana, M. Moreno-Manas, *Chem. Rev.* **2006**, 4622.

VIII.1. Heck coupling

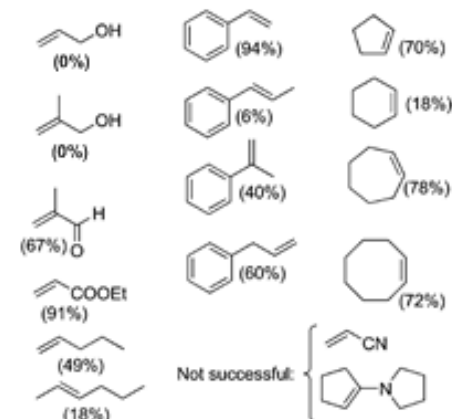
Scope: Diazonium salts<sup>28</sup>



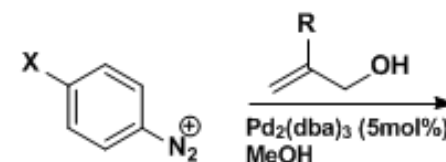
Ar = *o*-MeC<sub>6</sub>H<sub>4</sub>: 75 %  
Ar = *m*-MeC<sub>6</sub>H<sub>4</sub>: 30 %  
Ar = *p*-MeC<sub>6</sub>H<sub>4</sub>: 61 %  
Ar = *p*-OMeC<sub>6</sub>H<sub>4</sub>: 62 %  
Ar = *p*-COOMeC<sub>6</sub>H<sub>4</sub>: 62 %  
Ar = *o*-ClC<sub>6</sub>H<sub>4</sub>: 75 %  
Ar = *m*-ClC<sub>6</sub>H<sub>4</sub>: 78 %  
Ar = *p*-ClC<sub>6</sub>H<sub>4</sub>: 63 %  
Ar = *p*-BrC<sub>6</sub>H<sub>4</sub>: 14 %  
Ar = *p*-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>: 3 %  
Ar = *o*-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>: 0 %

Ar = 1-Naphthyl: 68 %  
Ar = 2-Naphthyl: 72 %

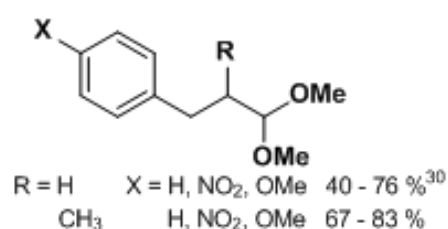
Olefins<sup>29</sup>



broad scope, exception NO<sub>2</sub>



broad scope, activated and non-activated olefins

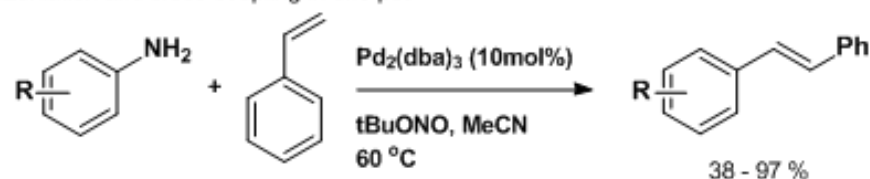


<sup>28</sup> K. Kikukawa, K. Nagira, N. Terao, F. Wada, T. Matsuda, *Bull. Chem. Soc. Jpn.* **1979**, 52, 2609.

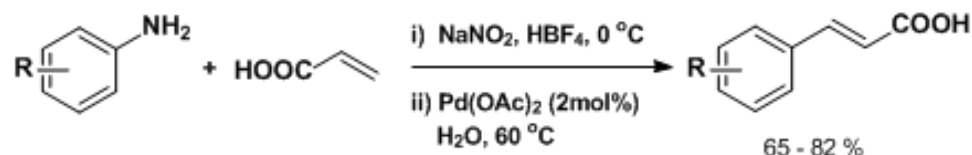
<sup>29</sup> K. Kikukawa, K. Nagira, F. Wada, T. Matsuda, *Tetrahedron* **1981**, 37, 31.

<sup>30</sup> J. Masllorens, S. Bouquillon, A. Roglans, F. Henin, J. Muzart, *J. Organomet. Chem.* **2005**, 3822.

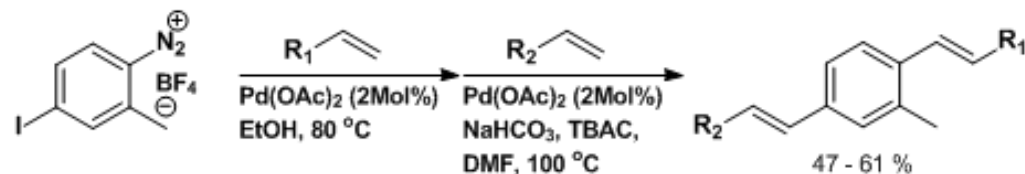
Diazonation and cross-coupling in one pot

R = Me, OMe, NO<sub>2</sub>, Cl, Br, I, naphthylF. Akiyama, H. Miyazaki, K. Kaneda, S. Teranishi, Y. Fujiwara, M. Abe, H. Taniguchi, *J. Org. Chem.* **1980**, 45, 2359.

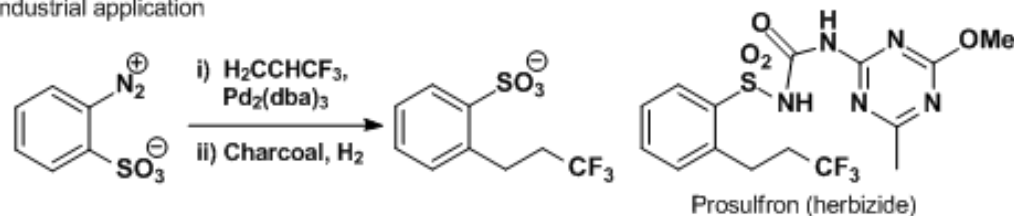
Reaction in water

S. Sengupta, S. Bhattacharyya, *J. Chem. Soc. Perkin Trans. 1* **1993**, 1943.

Chemoselective reaction

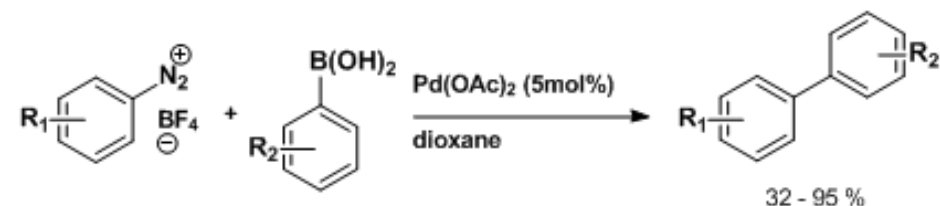
S. Sengupta, S. K. Sadhukhan, *Tet. Lett.* **1998**, 39, 715.

Industrial application

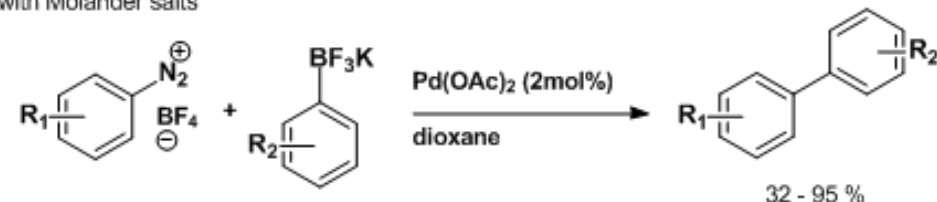


## VIII.2. Suzuki coupling

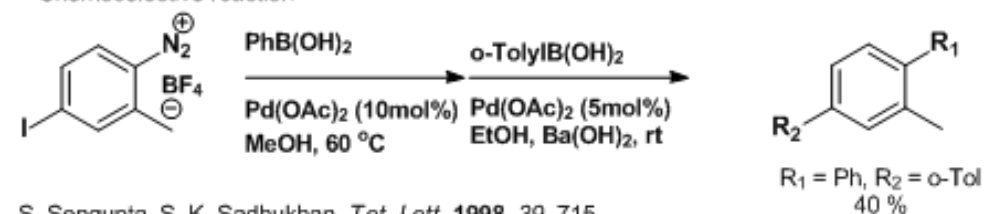
with boronic acids

R<sub>1</sub> = Me, Br, PhCO, OMe, COOEt, CN, NO<sub>2</sub>, OTf  
R<sub>2</sub> = F, Cl, OMe, Ar, naphthylS. Darses, T. Jeffery, J. P. Genet, J. L. Brayer, J. P. Demoute, *Tet. Lett.* **1996**, 37, 3857; S. Darses, T. Jeffery, J. L. Brayer, J. P. Demoute, *Bull. Soc. Chim. Fr.* **1996**, 133, 1095; S. Sengupta, S. Bhattacharyya, *J. Org. Chem.* **1997**, 62, 3405; S. Sengupta, S. K. Sadhukhan, *Tet. Lett.* **1998**, 39, 715.

with Molander salts

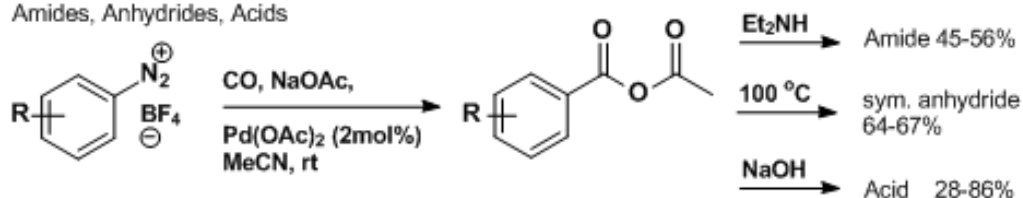
R<sub>1</sub> = Me, PhCO, OMe, COOEt, NO<sub>2</sub>, Br, F, I, OTf  
R<sub>2</sub> = F, Cl, OMe, SPh, PhCO, I, OTf, naphthylS. Darses, J. P. Genet, J. L. Brayer, J. P. Demoute, *Tet. Lett.* **1997**, 38, 4393; S. Darses, G. Michaud, J. P. Genet, *Eur. J. Org. Chem.* **1999**, 1875.

Chemoselective reaction

S. Sengupta, S. K. Sadhukhan, *Tet. Lett.* **1998**, 39, 715.

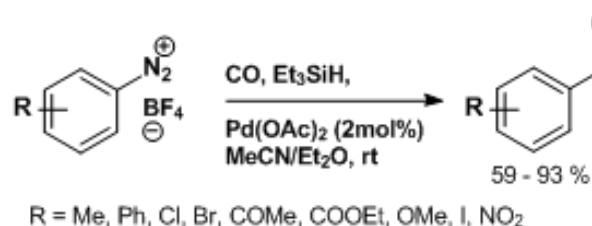
## VIII.3. Carbonylative coupling

Amides, Anhydrides, Acids



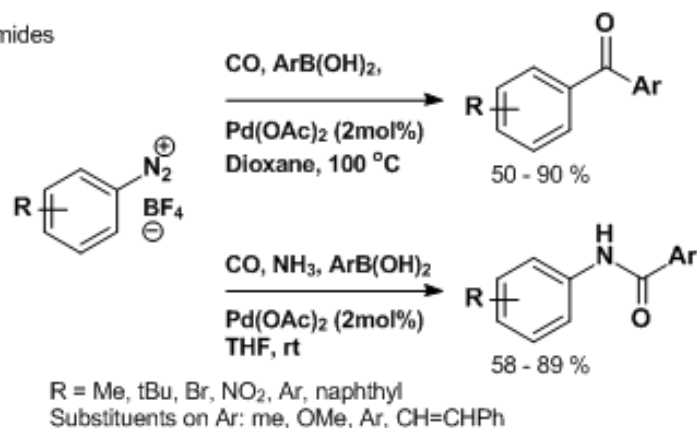
K. Nagira, K. Kikukawa, F. Wada, T. Matsuda, *J. Org. Chem.* **1980**, *45*, 2365; K. Kikukawa, K. Kono, K. Nagira, F. Wada, T. *Tet. Lett.* **1980**, *21*, 2877; K. Kikukawa, K. Kono, K. Nagira, F. Wada, T. Matsuda, *J. Org. Chem.* **1981**, *46*, 4413.

Aldehydes



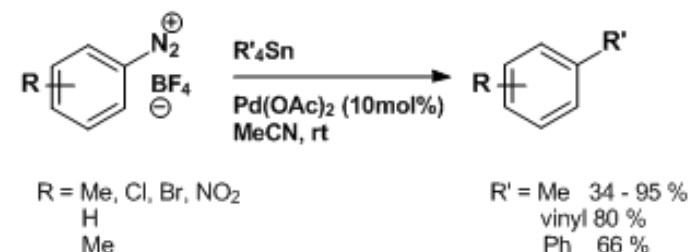
K. Kikukawa, T. Totoli, F. Wada, T. Matsuda, *J. Organomet. Chem.* **1984**, *270*, 283.

Ketones, Amides



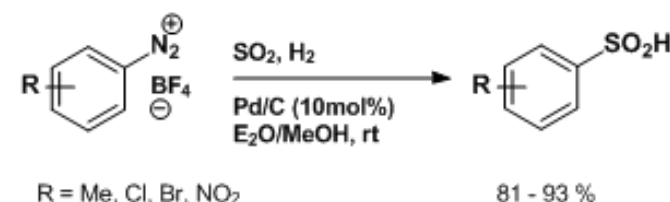
M. B. Andrus, Y. Ma, Y. Zang, C. Song, *Tet. Lett.* **2002**, *43*, 9137; Y. Ma, C. Song, Q. Chai, M. B. Andrus, *Synthesis* **2003**, 2886.

## VIII.4. Stille coupling

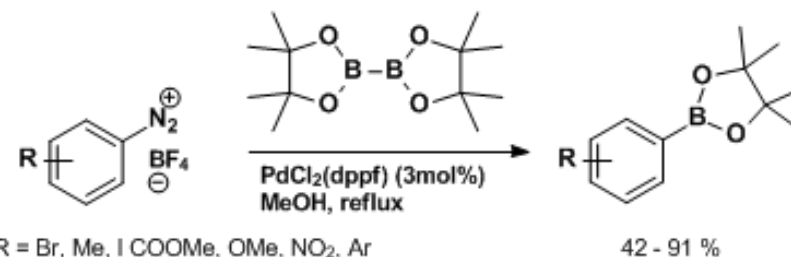


K. Kikukawa, K. Kono, F. Wada, T. Matsuda, *J. Org. Chem.* **1983**, *48*, 1333.

## VIII.5. Heteroatom coupling

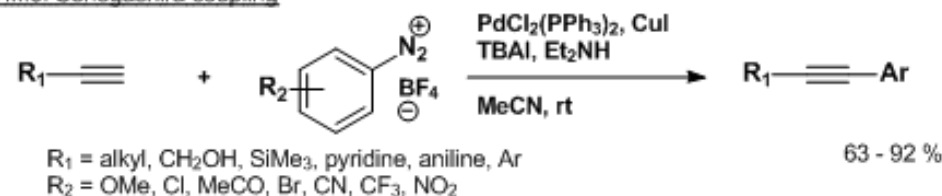


K. Kikukawa, T. Totoli, F. Wada, T. Matsuda, *J. Organomet. Chem.* **1984**, *270*, 283; L. S. Varnedoe, B. D. Angel, J. L. McClellan, J. M. Hanna Jr., *Lett. Org. Chem.* **2010**, *7*, 1

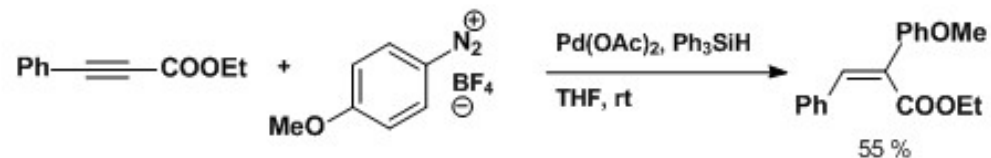


D. M. Willis, R. M. Strongin, *Tet. Lett.* **2000**, *41*, 8683.

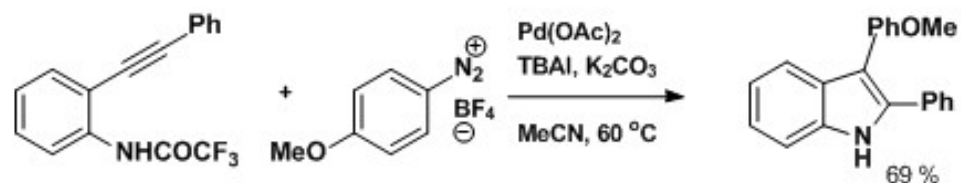
## VIII.6. Sonogashira coupling



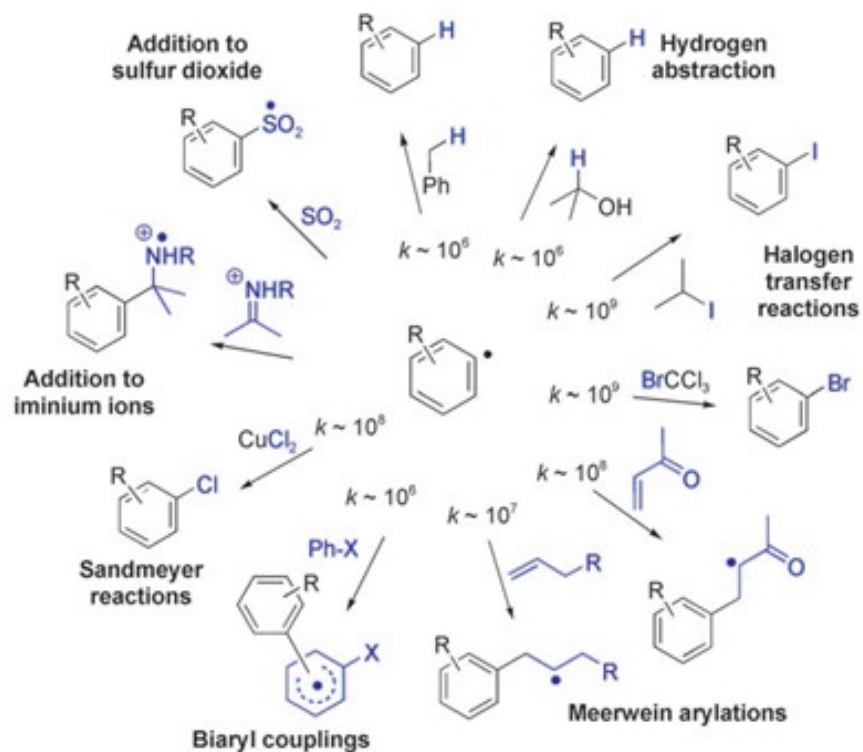
G. Fabrizi, A. Goggiani, A. Sferrazza, S. Cacchi, *Angew. Int. Ed.* **2010**, *49*, 4067.



S. Cacchi, G. Fabrizi, A. Goggiamani, D. Persiani, *Org. Lett.* **2008**, *10*, 1597.



S. Cacchi, G. Fabrizi, A. Goggiamani, D. Perboni, A. Sferrazza, P. Stabile, *Org. Lett.* **2010**, *12*, 3279.



M. R. Heinrich, *Chem. Eur. J.* **2009**, *15*, 820.