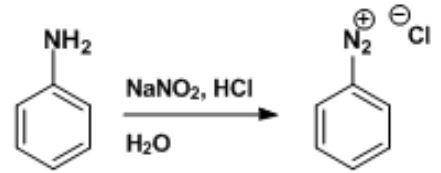
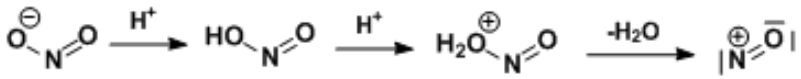
T. Brueckl

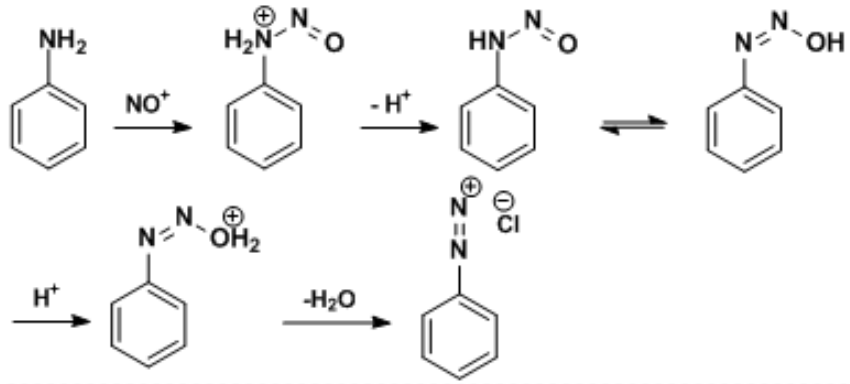
Aryldiazonium Chemistry

Baran Group Meeting
02-05-2011

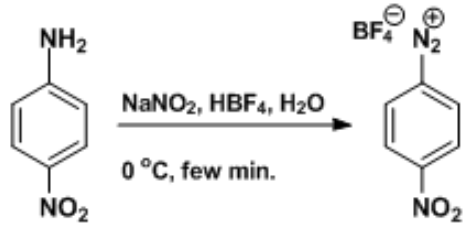
I. Diazotation, Diazoniation, or Diazotization

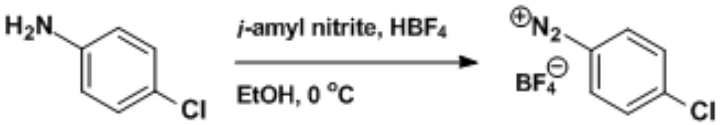


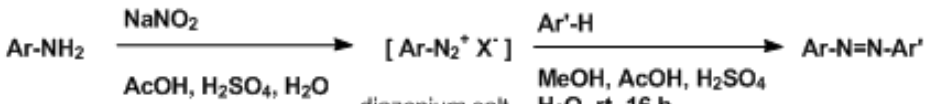




Examples:

1) 

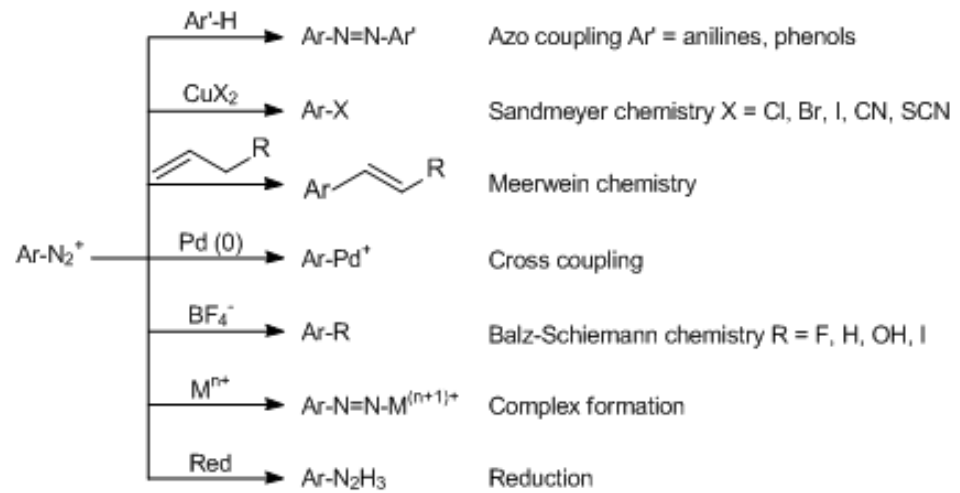
2) 

3) 

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.

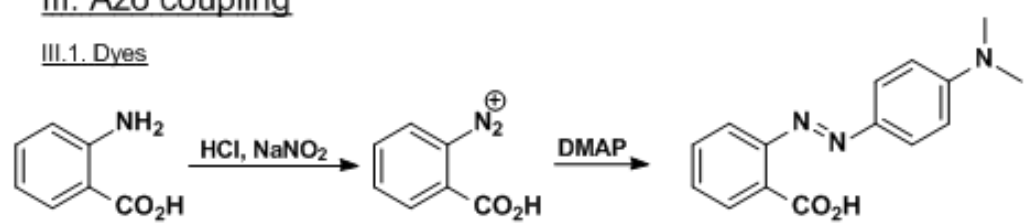
First Synthesis:
P. Griess, *Ann.* **1858**, *106*, 123.

II. Summary of reaction pathways



III. Azo coupling

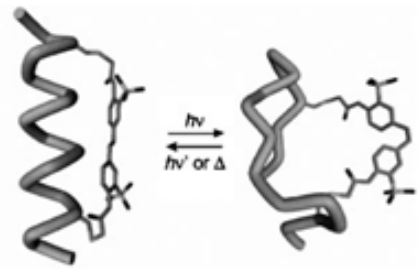
III.1. Dyes



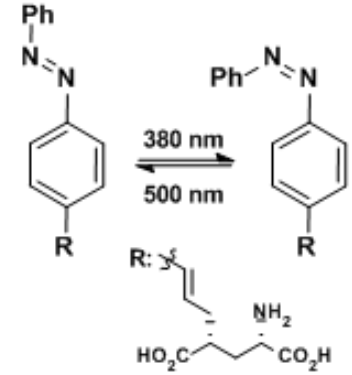
Methyl Red

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



trans-Azo *cis*-Azo



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.

T. Brueckl

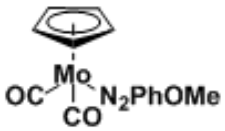
Aryldiazonium Chemistry

Baran Group Meeting
02-05-2011

IV. Complex formation

ArN_2^+ is isoelectronic with CO, NO^+, and RNC.
Numerous ArN_2^+ - transition metal complexes have been isolated.

Reviews:
R. B. King, *J. Organomet. Chem.* **1995**, 187.
D. Sutton, *Chem. Rev.* **1993**, *93*, 995.



First isolated complex

V. Reduction

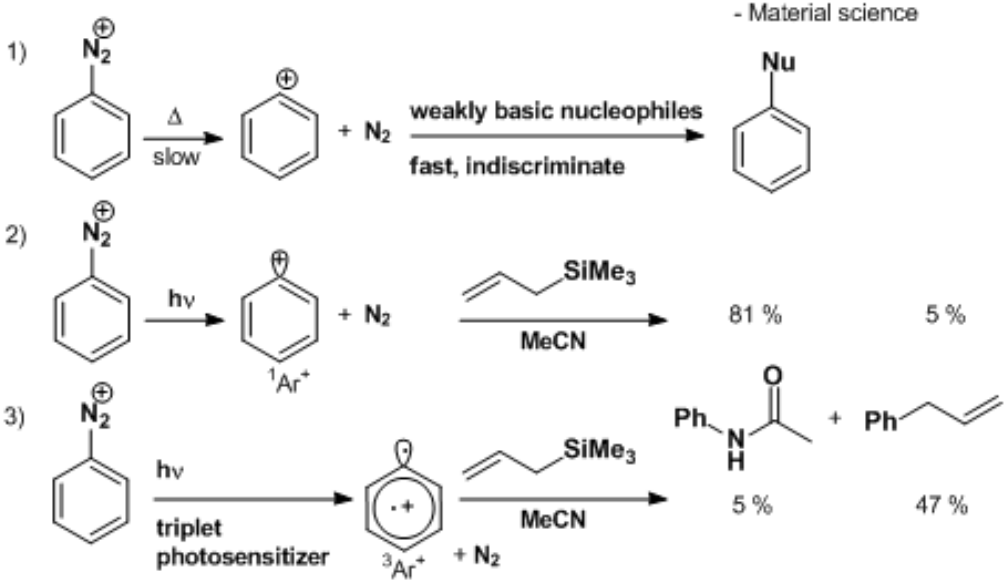
J. R. Robinson, N. E. Good, *Can. J. Chem.* **1957**, *35*, 1578.

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

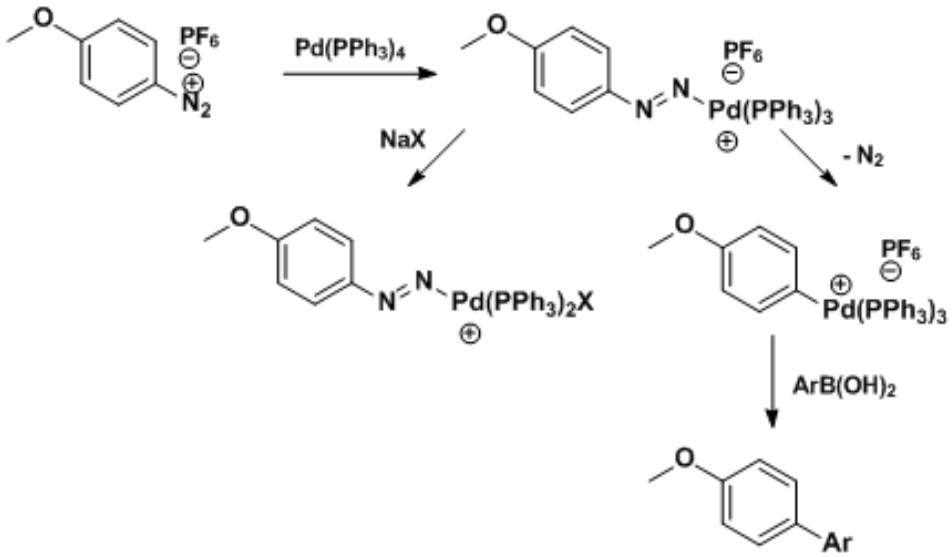
VI. Dediazoniation

VI.1. Heterolytic C-N bond cleavage

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



Dediazoniation by palladium



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

VI.2. Mixed processes - Solvolysis

Homolytic

high nucleophilicity of the solvent (py, HMPT)
electronwithdrawing substituents

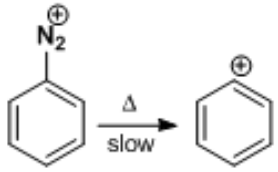
$ArN_2^+ + :ED \longrightarrow Ar\text{-}N{=}N\text{-}ED^+$

$\longrightarrow Ar\cdot + N_2 + \cdot ED^+$

in acidic methanol: under O_2 exclusion

Heterolytic

low nucleophilicity of solvent (H_2O, DCM)
electrondonating substituents



when O_2 is present

I. Szele, H. Zollinger, *Helv. Chim. Acta* **1978**, *61*, 1721.
D. F. DeTar, M. N. Turetzky, *JACS* **1955**, *77*, 1745.

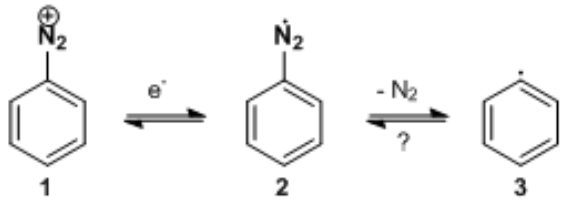
T. Brueckl

Aryldiazonium Chemistry

Baran Group Meeting
02-05-2011

VI.3. Homolytic Dediazoniation

General considerations



$k = 10^5\ s^{-1}$ Ref 1

Experimental evidence for electrontransfer:

- Electrochemical:[2] electronwithdrawing substituents facilitate reduction - stabilize **2**.
  electrondonating substituents impede reduction - stabilize **1**.
- Photoinduction:[3] rate of electrontransfer from pyrene to ArN_2^+ was measured.
- Pulse radiolysis: - Ar-N=N-N=N-Ar was detected.[4]
  - Alcohols sustain a radical-chain mechanism of reduction.[5]

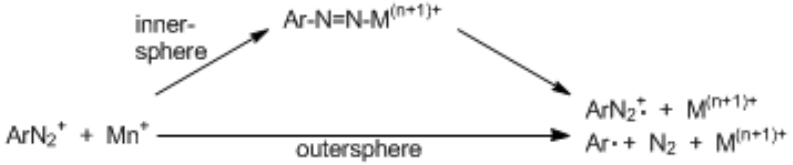
Electrontransfer:

$$ArN_2^+ + e^- \longrightarrow ArN_2^{\bullet} \longrightarrow Ar\bullet + N_2 \longrightarrow ArH + \bullet RH$$

$$RH\bullet + ArN_2^+ \longrightarrow Ar\bullet + N_2 + R + H^+$$

Dediazoniation by metal ions[1]

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.



[1] Summary in C. Galli, *Chem. Rev.* **1988**, *88*, 765 (p. 769f for kinetics and p. 771f for metal cat.).
[2] R. M. Elofson, F. F. Gadallah, J. Org. Chem. 1969, 34, 854.
[3] H. G. O. Becker, R. Ebisch, G. Israel, G. Kroha, W. Kroha, O. Brede, R. Mehnert, *J. Prakt. Chem.* **1977**, *319*, 98.
[4] O. Brede, R. Mehnert, W. Naumann, H. G. O. Becker, *Radiochem. Radioanal. Lett.* **1979**, *39*, 247.
[5] E. S. Lewis, D. J. Chambers, *JACS* **1971**, *93*, 3267.

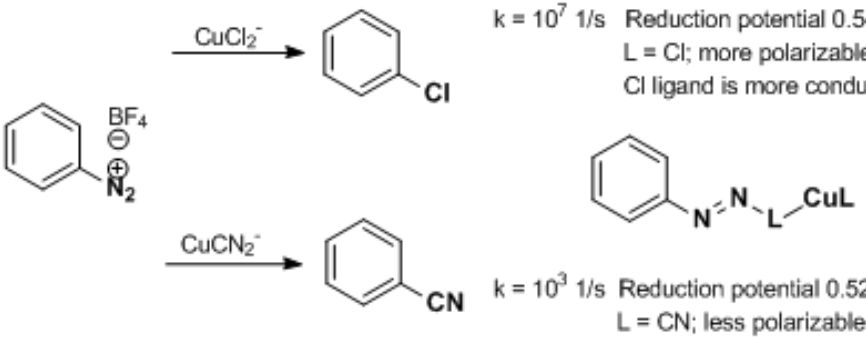
inner-sphere
Complex with Diazonium compound is formed

examples:
Phenothiazine
Sandmeyer chemistry

outer-sphere
no complex is formed

examples:
Phenothiazine
Hydroquinone

Sandmeyer chemistry[6]

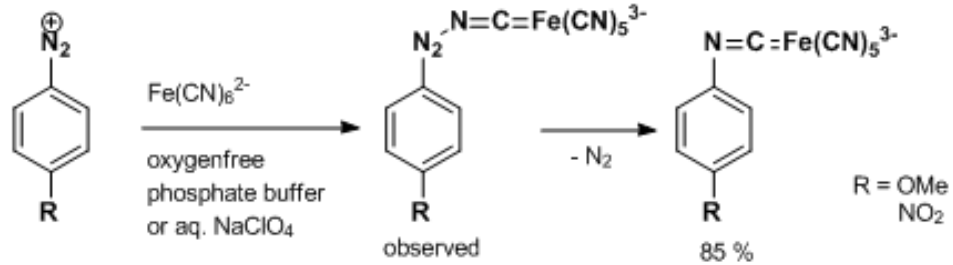


$k = 10^7$ 1/s Reduction potential 0.54 V
L = Cl; more polarizable σ-orbital
Cl ligand is more conductive than CN

$k = 10^3$ 1/s Reduction potential 0.52 V
L = CN; less polarizable sp-orbital
CN ligand is less conductive than Cl

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

Still ongoing discusson
$Fe(CN)_6^{4-}$ was believed to react *via* an outer-sphere mechanism,[7] but:[8]



In oxygen-containing solutions phenol is obtained.

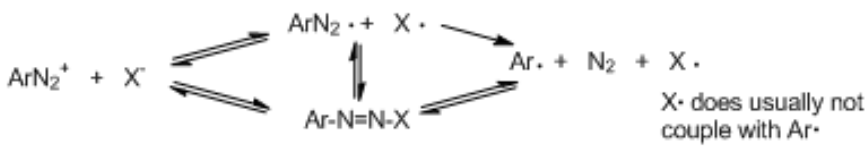
[6] P. Hanson, S. C. Rowell, J. R. Jones, P. H. Walton, A. W. Timms, *J. Chem. Soc., Perkin Trans. 2* **2002**, 1126.
[7] M. P. Doyle, J. K. Guy, K. C. Brown, S. N. Mahapatro, C. M. VanZyl, J. R. Pladziewicz, *JACS* **1987**, *109*, 1536.
[8] U. Klaening, T. Lund, H. Lund, S. U. Pedersen, K. Daasbjerg, *J. Phys. Chem. A* **2010**, *114*, 6575.

T. Brueckl

Aryldiazonium Chemistry

Baran Group Meeting
02-05-2011

Dediazoniation by anions[9]

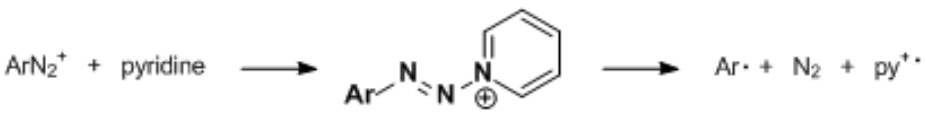


inner-sphere
low dielectric constant of solvent

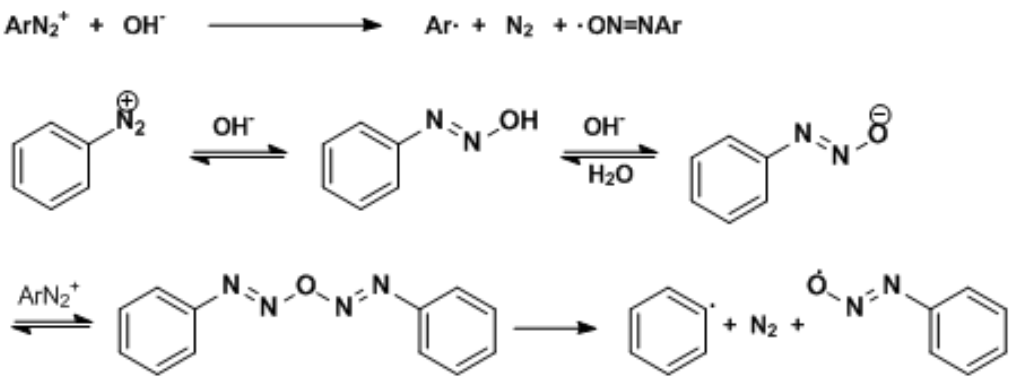
examples:
ArS^-, OH^- RO^-, pyridine

outer-sphere
suitable redox potential

examples:
I^-, Br^-, ArS^-, Xanthate, Amines, $H_2PO_3^-$



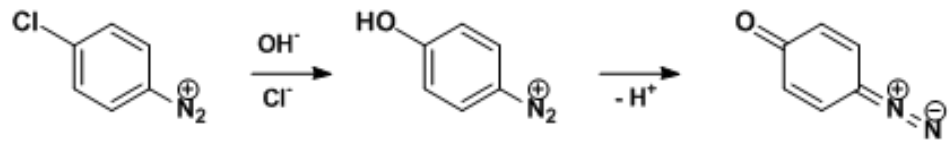
Gomberg-Bachmann Reaction[10]



Fluorine
Anions, which are not good electrondonors can lead to a heterolytic pathway.

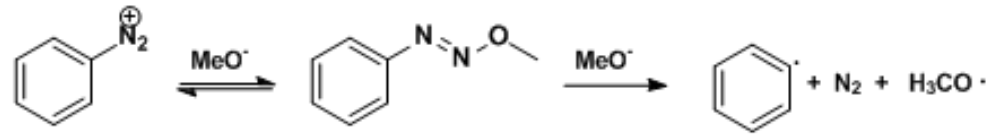
[9] Summary in C. Galli, *Chem. Rev.* **1988**, *88*, 765 (p. 773f).
[10] M. Gomberg, W. E. Bachmann, *JACS* **1924**, *46*, 2339.

Nucleophilic aromatic substitution[11]

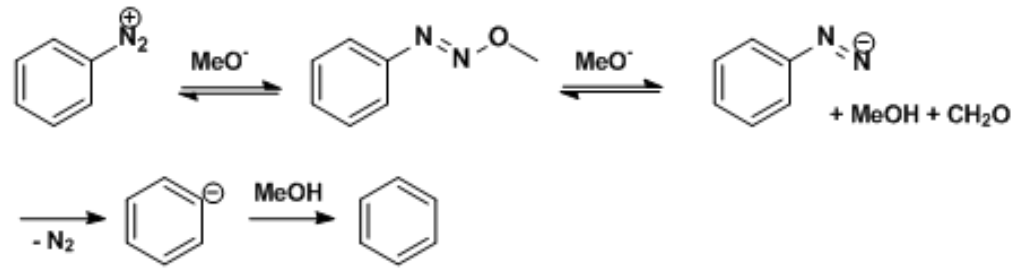


Methanolate[12]

basic conditions



strongly basic conditions (heterolytic)



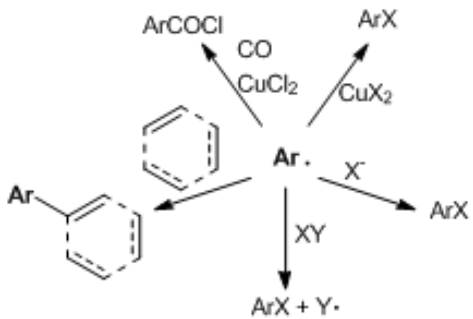
[11] J. Besse, W. Schwarz, H. Zollinger, *Helv. Chim. Acta* **1981**, *64*, 504.
[12] T. J. Broxton, J. F. Bunnett, C. H. Paik, *J. Org. Chem.* **1977**, *42*, 643.

T. Brueckl

Aryldiazonium Chemistry

Baran Group Meeting
02-05-2011

VII. Reactions of the Arylradical



Cu-catalyzed Sandmeyer chemistry

Coupling with a nucleophile

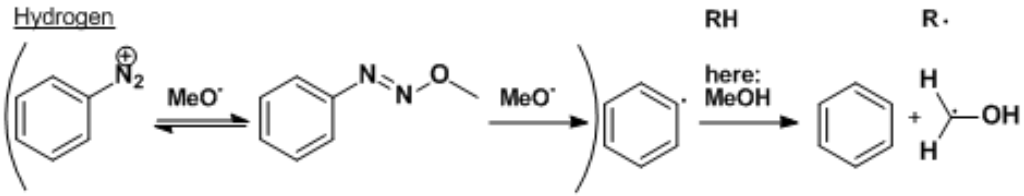
Atom transfer

Addition to a π-system

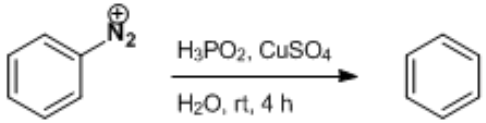
Coupling with CO/SO_2

VII.1. Atom transfer

Hydrogen



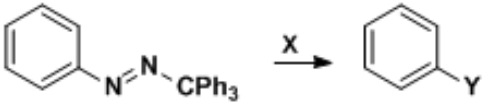
Often the main product as a hydrogen atom can be transfered from the solvent.
$k = 10^5$ to 10^6 1/s



Hydro-dediazoniation is best performed with hypophosphorous acid under Cu-catalysis.[13]

$ArN_2^+ + H_2PO_2^- \rightarrow Ar\cdot + N_2 + \cdot H_2PO_2$
$Ar\cdot + H_3PO_2 \rightarrow ArH + \cdot H_2PO_2$
$H_2PO_2\cdot + ArN_2^+ \rightarrow Ar\cdot + N_2 + H_2PO_2^+$
$H_2PO_2^+ + H_2O \rightarrow H_3PO_3 + H^+$

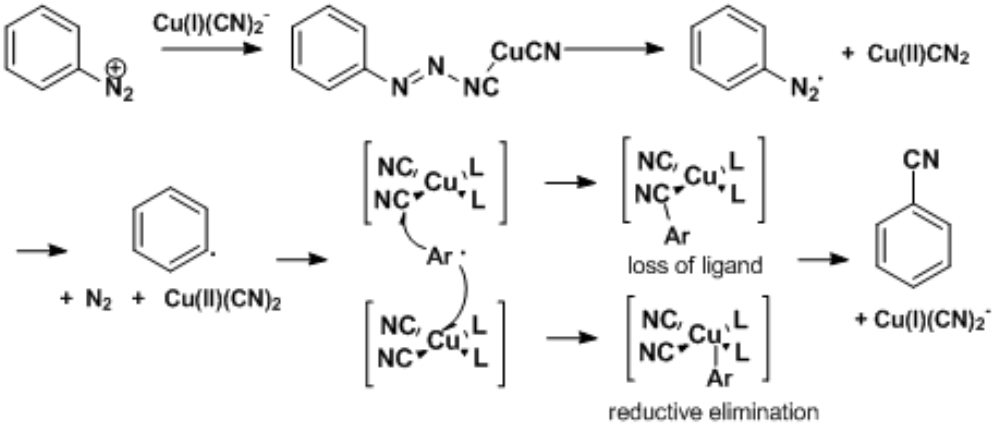
Halogens



X[14]	k	Y
MeOH	$5x10^5$	H
tert-alkyl	$2x10^6$	H
I_2	$1x10^{10}$	I
ArI	$9x10^7$	I
CBr_4	$5x10^9$	Br
PhH	$1x10^6$	Ph
Ethylen	$8x10^6$	CH_2CH_3

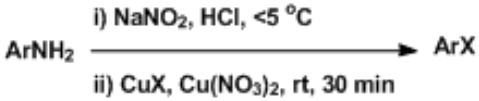
[13] N. Kornblum, G. D. Cooper, J. E. Taylor, *JACS* **1950**, *72*, 3013.
[14] R. G. Kryger, J. P. Lorand, N. R. Stevens, N. R. Herron, *JACS* **1977**, *99*, 7589.

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:



X = Cl, Br, I

The reaction can be improved by addition of poly(ethylene glycols)[15] or crown ethers.[16]

Nucleophiles used in Sandmeyer chemistry: Cl^-, Br^-, I^-, CN^-, NO_2^-, OH^-
Nucleophiles not used: SO_4^{2-}, ClO_4^-, NO_3^-

T. Cohen, A. G. Dietz, J. R. Miser, *J. Org. Chem.* **1977**, *42*, 2053.

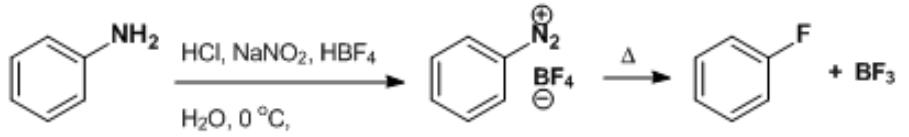
P. Hanson, S. C. Rowell, J. R. Jones, P. H. Walton, A. W. Timms, *J. Chem. Soc., Perkin Trans. 2* **2002**, 1126 (Mechanism).
[15] N. Suzuki, Y. Kaneko, T. Nomoto, Y. Izawa, *Chem. Comm.* **1984**, 1523.
[16] R. A. Bartach, H. Chen, N. F. Haddock, P. N. Juri, *JACS* **1976**, *98*, 6753.

T. Brueckl

Aryldiazonium Chemistry

Baran Group Meeting
02-05-2011

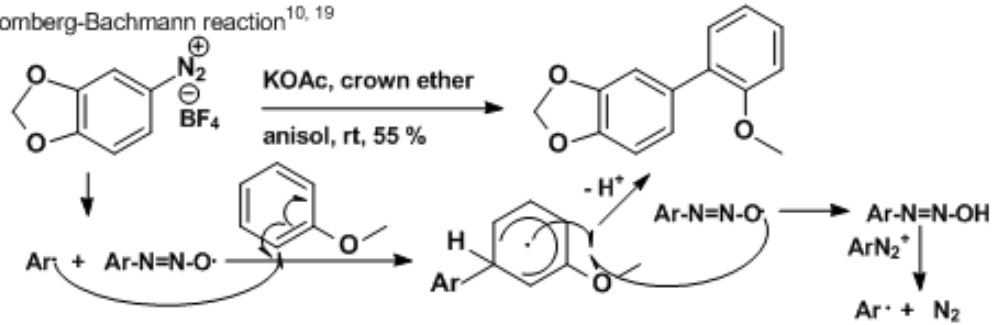
Insertion: Balz-Schiemann Reaction[17]



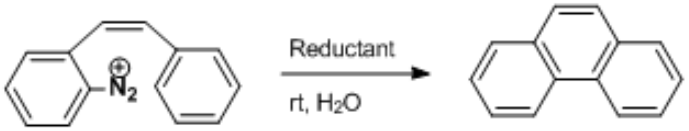
Sandmeyer conditions will not yield fluorinated aryls due to the high oxidation potential of F^- and the inefficiency of the transfer of the fluoride ligand from the copper salt.
In absence of BF_4^- phenols can be prepared.
Other arylhalogenides are available by this procedure, but Sandmeyer conditions are superior.[18]

VII.3. Addition to aromatic systems

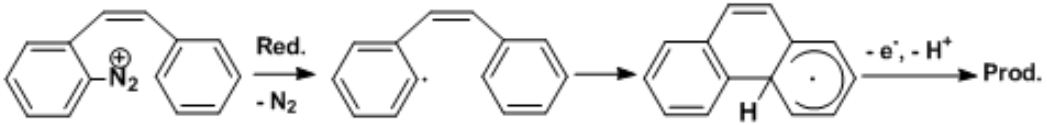
Gomberg-Bachmann reaction[10, 19]



Pschorr reaction[20]

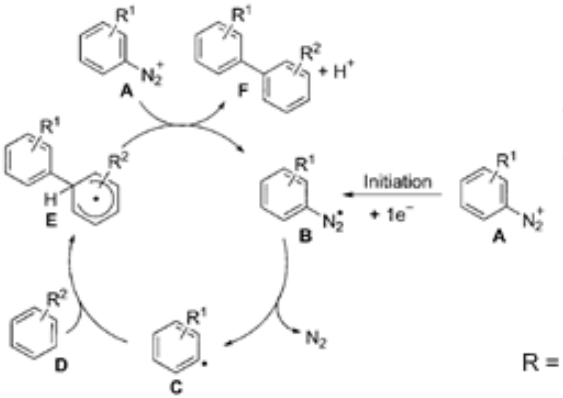


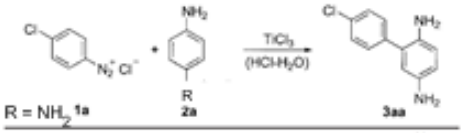
Reductants: Cu(I) salts, I^-, pyridine, hypophophoric acid,[21] Fe(II) salts[22]



[17] D. T. Flood, *Org. Synth. Coll. Vol. 2* **1943**, 295; R. A. Abramovitch, J. G. Saha, *Can. J. Chem.* **1965**, *43*, 3269.
[18] G. A. Ohla, W. S. Tolgyesi, *J. Org. Chem.* **1961**, *26*, 2053.
[19] J. J. Li, Name Reactions, Springer (Berlin) **2009**, 262.
[20] R. Pschorr, *Chem. Ber.* **1896**, *29*, 496.
[21] C. Galli, *Chem. Rev.* **1988**, *88*, 765 (p. 781).
[22] F. W. Wassmundt, W. F. Kiesman, *J. Org. Chem.* **1995**, *60*, 196.

Recent arylations

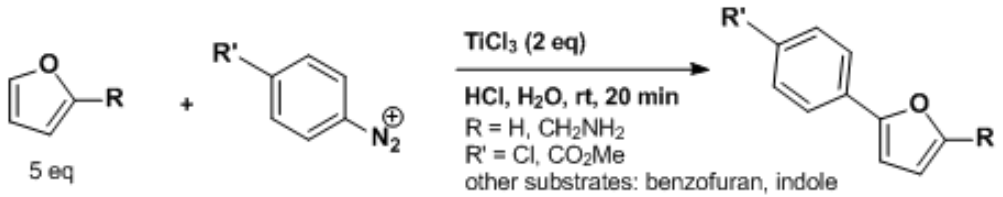




Entry	Equiv $TiCl_3$ (relative to 1a)	Addition of 1a over x min	3aa[a] Yield [%][b]/[%][c]
1	2.5	0	56/54
2	2.5	3	59/–
3	2.5	6	65/58
4	2.5	11	54/–
5	2.5	23	50/–
6	1.0	6	65/–
7	0.5	6	70/70
8	0.25	6	71/–
9	0.0	6	66/64

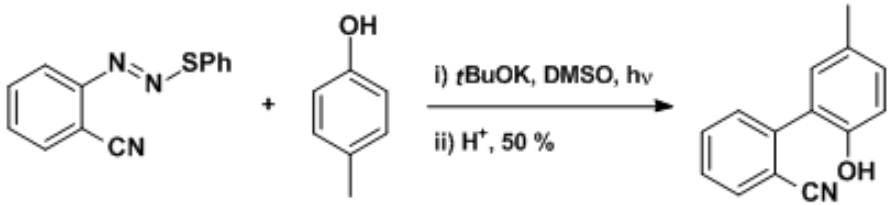
R = NH_2, OMe, OH, F, Cl, CO_2Me, COMe, Alkyl

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

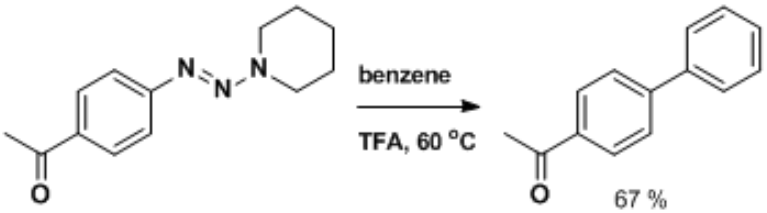


A. Wetzel, G. Pratsch, R. Kolb, M. R. Heinrich, *Chem. Eur. J.* **2010**, *16*, 2547.

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.

T. Brueckl

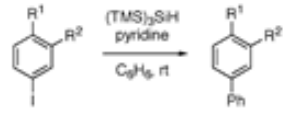
Aryldiazonium Chemistry

Baran Group Meeting
02-05-2011

Some informative examples not based on aryldiazonium salts

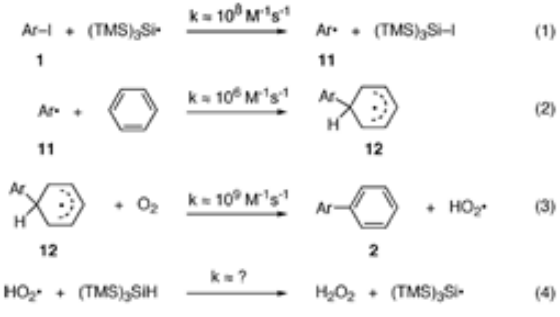
In modern variations aryl radicals are generated from aryl hydrazines,[23] and grignard reagents,[24] or from halides using organotin, organosilicon, or samarium compounds.[25] And Carboxylic and boronic acids.[26]

- Oxidation of the coupling product performed by oxygen[27]

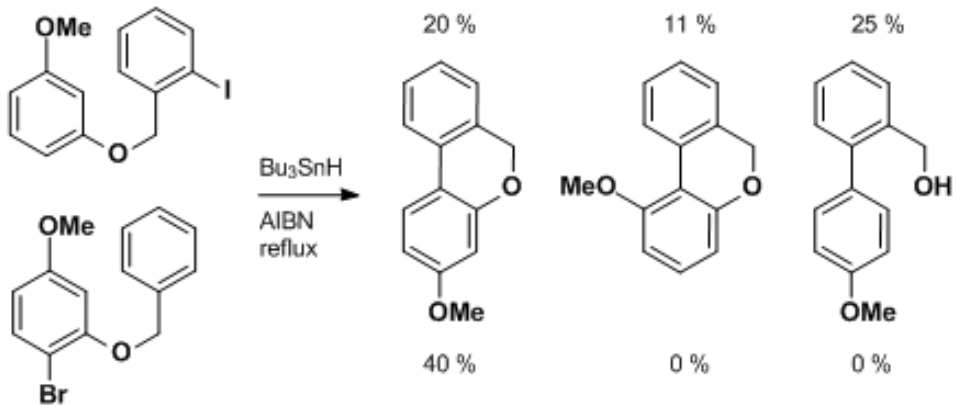


entry	aryl iodide	R^1	R^2	product	% yield[b]
1	**1a**	CO_2Me	H	**2a**	87
2	**1b**	H	H	**2b**	75
3	**1c**	OMe	H	**2c**	90
4	**1d**	H	CO_2Et	**2d**	82
5	**1e**	t-Bu	H	**2e**	90
6	**1f**	H	OMe	**2f**	89

[a]rxn conds: **1**, $(TMS)_3SiH$ (1.2 equiv), and pyridine (5 equiv) were dissolved in benzene (50 mL, 4 mM); [b]isolated yields

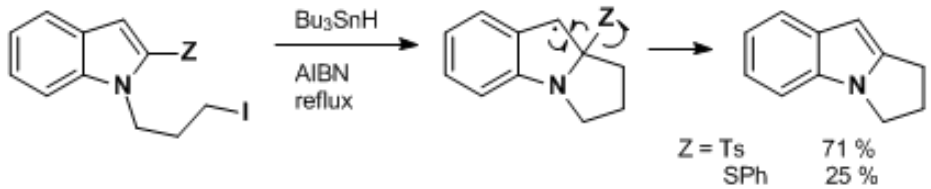


- 5-ring formation (5-exo) prefered to 6-ring formation (6-endo).



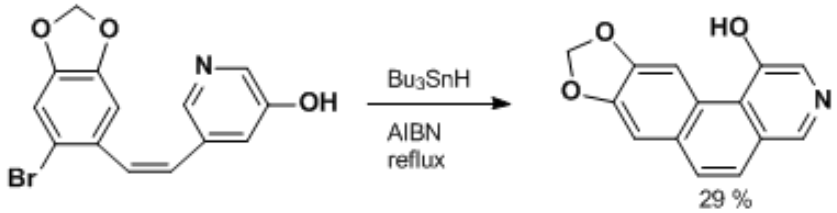
[23] A. S. Demir, O. Reis, E. Oezguel-Karaaslan, *J. Chem. Soc. Perkin Trans. 1* **2001**, 3042.
[25] W. R. Bowman, J. M. D. Storey, *Chem. Soc. Rev.* **2007**, *36*, 1803; D. P. Curran, A. I. Keller, *JACS* **2006**, *128*, 13706.
[26] I. B. Seiple, S. Su, R. A. Rodriguez, R. Gianatassio, Y. Fujiwara, A. L. Sobel, P. S. Baran, *JACS* **2010**, *132*, 13194.
[27] W. R. Bowman, E. Mann, J. Parr, *J. Chem. Soc. Perkin Trans. 1* **2000**, 2991.

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



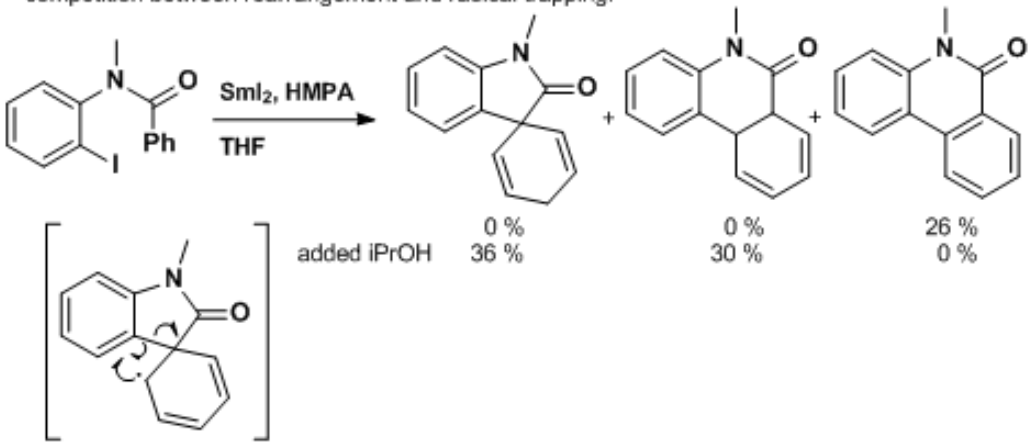
S. Caddick, K. Abutayab, K. Jenkins, R. I. West, *J. Chem. Soc. Perkin Trans. 1* **1996**, 675.

- Synthesis of heterocycles (Toddaquinoline).



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.

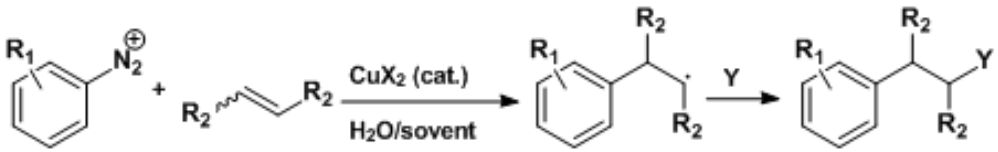
T. Brueckl

Aryldiazonium Chemistry

Baran Group Meeting
02-05-2011

VII.3. Addition to olefins

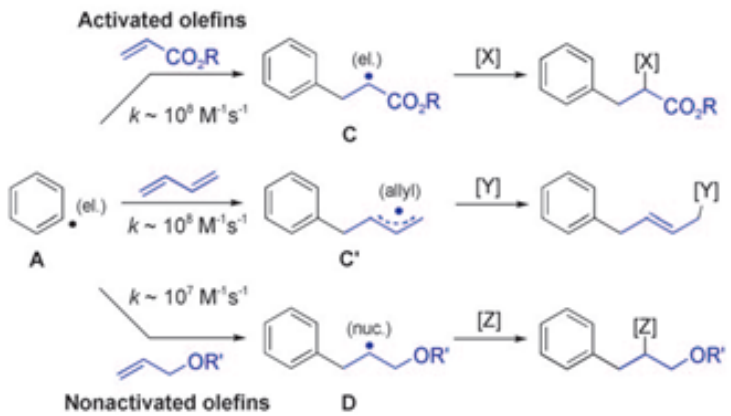
Meerwein reaction



R_1 = H, alkyl, O-alkyl, Cl, Br, I, CO_2-alkyl, CONHR, SO_2R, NO_2, CF_3
R_2 = H, alkyl, aryl, CHO, CO-alkyl, CO_2-alkyl, CO_2H, CO_2NH_2, CO_2NR_2, CN, alkenyl, Cl, Br
X = Cl, Br
Y = H, ArN_2^+, OR, SR, Cl, Br, I, CN
solvent: acetone, MeCN

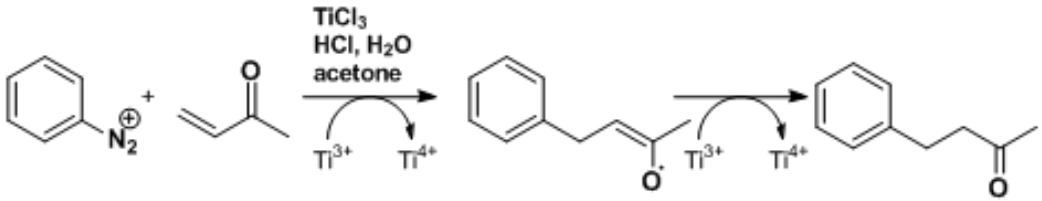
Three classes of Meerwein arylation sustrates:
1) Activated olefins - acceptor-substituted or conjugated olefins
2) Non-activated olefins - only sp^3-carbons adjacent to double bond
3) Borderline cases - e.g. vinyl ethers, vinyl halogenides, vinyl trifluoromethanes

Activated olefins	**Non-activated olefins**
usual substrates	
fast addition to the aryl radical	relatively slow addition to aryl radical
can undergo polymerisations	do not polymerise
form electrophilic radical	form nucleophilic radical
use nucleophilic trapping agent	use electrophilic trapping agent
(Sandmeyer product formation possible)	(Sandmeyer product formation unlikely)



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

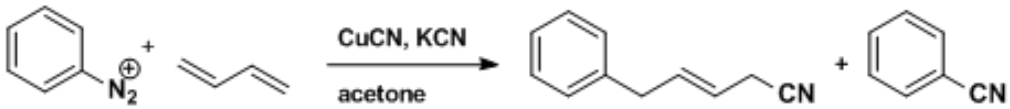
Trapping by Hydrogen - Ti(III)-catalyzed Meerwein reaction



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

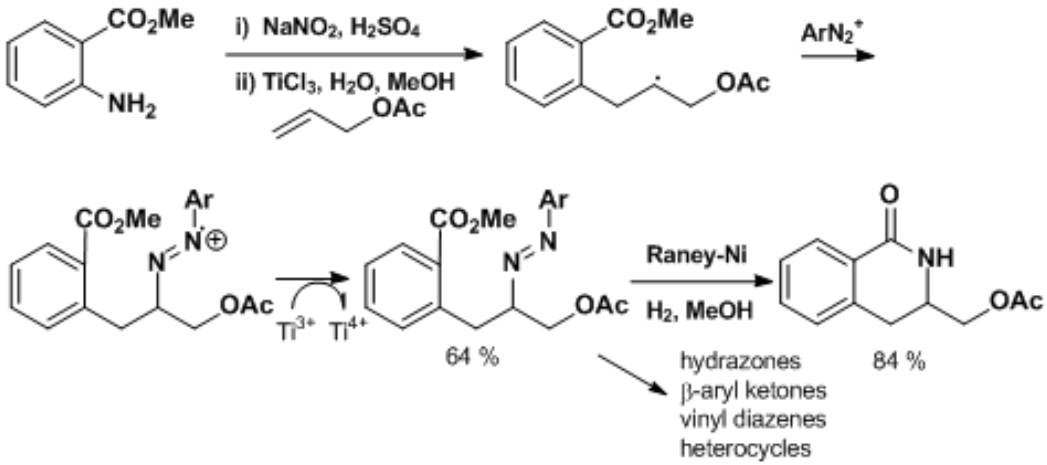
A. Citterio et al. *Synthesis* **1980**, 291; *Synthesis* **1986**, 308.
H. I. Tashtoush, R. Sustmann, *Chem. Ber.* **1993**, *126*, 1759.

Trapping by CN - Carbocyanation



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

Trapping with Aryldiazonium ion - Carboamination

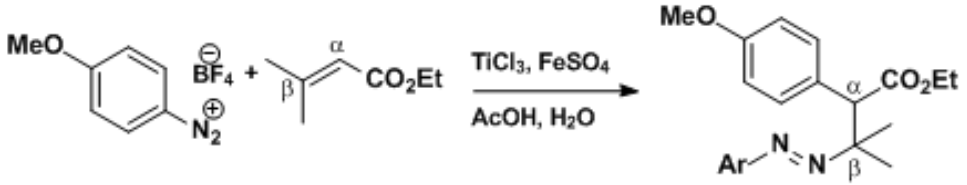


M. R. Heinrich, O. Blank, S. Woelfel, *Org. Lett.* **2006**, *8*, 3323.

T. Brueckl

Aryldiazonium Chemistry

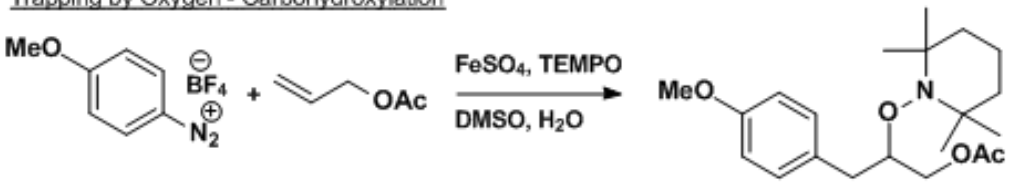
Baran Group Meeting
02-05-2011

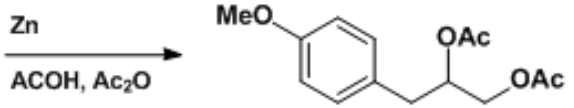


Sterically hindered β-position induces attack of the radical in the α-position.

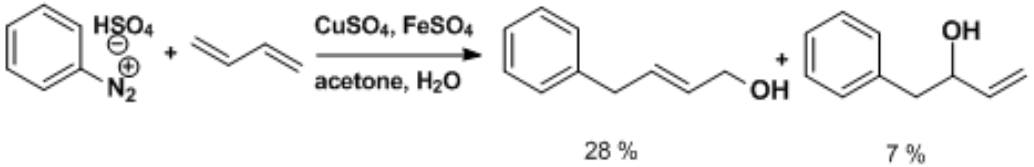
A. Citterio, F. Minisci, A. Albinati, S. Bruckner, *Tet. Lett.* **1980**, 2909.

Trapping by Oxygen - Carbohydroxylation



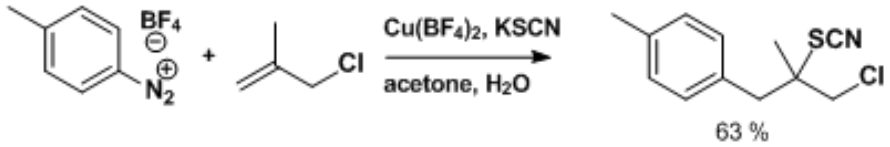


M. R. Heinrich, A. Wetzel, M. Kirschstein, *Org. Lett.* **2007**, *9*, 3833.

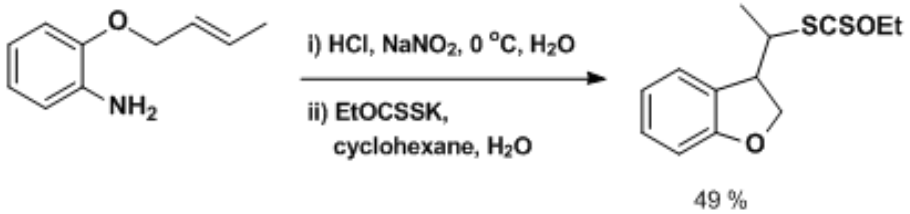


M. R. Heinrich, *Chem. Eur. J.* **2009**, *15*, 820; N. I. Ganushchak, B. D. Grishchuk, A. V. Dombrovskii, *Zh. Org. Khim.* **1973**, *9*, 1030 (paper cited in Heinrich review).

Trapping by Sulfur - Carbothionylation

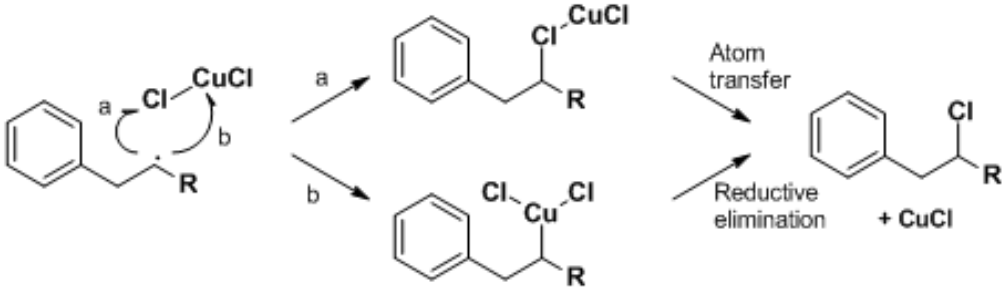


M. R. Heinrich, *Chem. Eur. J.* **2009**, *15*, 820; P. M. Gorbovoi, G. N. Tulaidan, B. D. Grishchuk, *Russ. J. Gen. Chem.* **2008**, *78*, 133 (paper cited in Heinrich review).



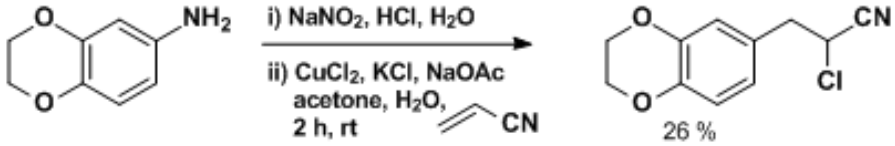
L. Tournier, Z. Zard, *Tet. Lett.* **2005**, *46*, 971.

Trapping by Chlorine - Carbochlorination



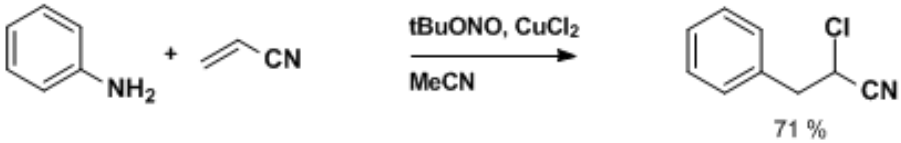
H. Brunner, C. Buechel, M. P. Doyle, *J. Organomet. Chem.* **1997**, *541*, 89.

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. Siegried, R. C. Elliot, J. F. Dellaria Jr, *J. Org. Chem.* **1977**, *42*, 2431.

T. Brueckl

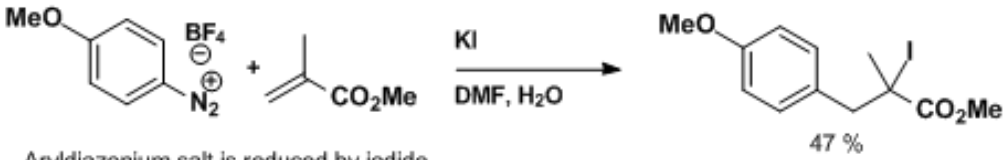
Aryldiazonium Chemistry

Baran Group Meeting
02-05-2011

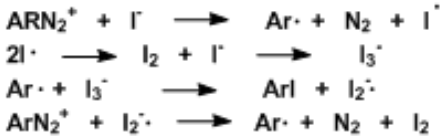
Trapping by Bromine - Carbobromination

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

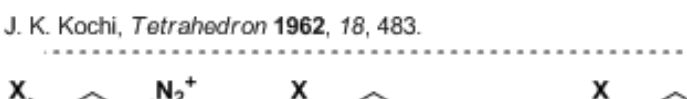


Aryldiazonium salt is reduced by iodide.

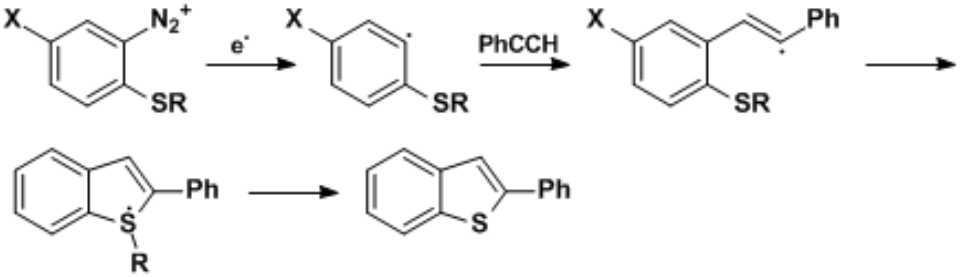


C. Galli, *Chem. Rev.* **1988**, *88*, 765
M. R. Heinrich, *Chem. Eur. J.* **2009**, *15*, 820.

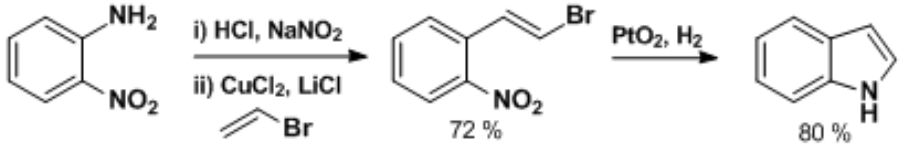
Related reactions



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



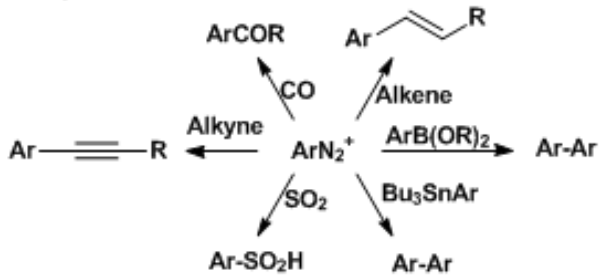
R. Leardini, G. F. Pedulli, A. Tundo, G. Zanardi, *Chem. Comm.* **1985**, 1390.



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

VIII. Pd-catalyzed cross-coupling

Summary:

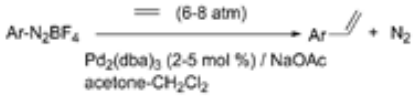


Carbonylative coupling
Heck coupling
Suzuki coupling
Stille coupling
Heteroatom coupling
Sonogashira coupling

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

VIII.1. Heck coupling

Scope: Diazonium salts[28]



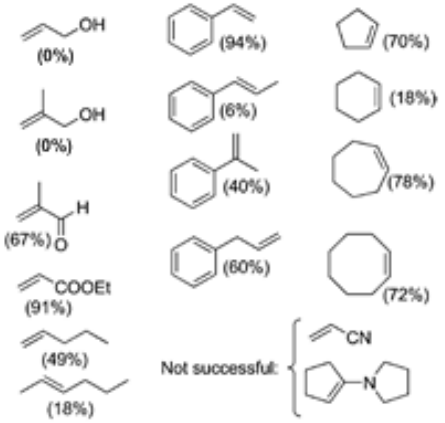
Ar = *o*-MeC_6H_4: 75 %
Ar = *m*-MeC_6H_4: 30 %
Ar = *p*-MeC_6H_4: 61 %
Ar = *p*-$OMeC_6H_4$: 62 %
Ar = *p*-$COOMeC_6H_4$: 62 %

Ar = *o*-ClC_6H_4: 75 %
Ar = *m*-ClC_6H_4: 78 %
Ar = *p*-ClC_6H_4: 63 %
Ar = *p*-BrC_6H_4: 14 %
Ar = *p*-$NO_2C_6H_4$: 3 %
Ar = *o*-$NO_2C_6H_4$: 0 %

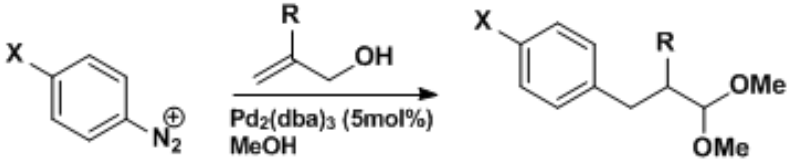
Ar = 1-Naphthyl: 68 % Ar = 2-Naphthyl: 72 %

broad scope, exception NO_2

Olefins[29]



broad scope, activted and non-activated olefins



R = H X = H, NO_2, OMe 40 - 76 %[30]
CH_3 H, NO_2, OMe 67 - 83 %

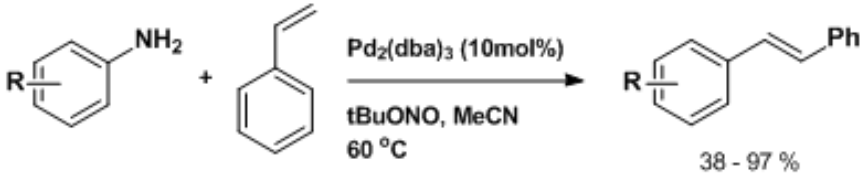
[28] K. Kikukawa, K. Nagira, N. Terao, F. Wada, T. Matsuda, *Bull. Chem. Soc. Jpn.* **1979**, *52*, 2609.
[29] K. Kikukawa, K. Nagira, F. Wada, T. Matsuda, *Tetrahedron* **1981**, *37*, 31.
[30] J. Masllorens, S. Bouquillon, A. Roglans, F. Henin, J. Muzart, *J. Organomet. Chem.* **2005**, 3822.

T. Brueckl

Aryldiazonium Chemistry

Baran Group Meeting
02-05-2011

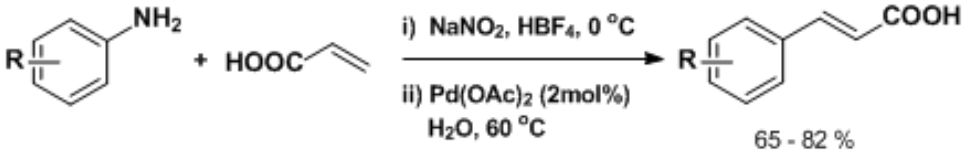
Diazoniation and cross-coupling in one pot



R = Me, OMe, NO_2, Cl, Br, I, naphthyl

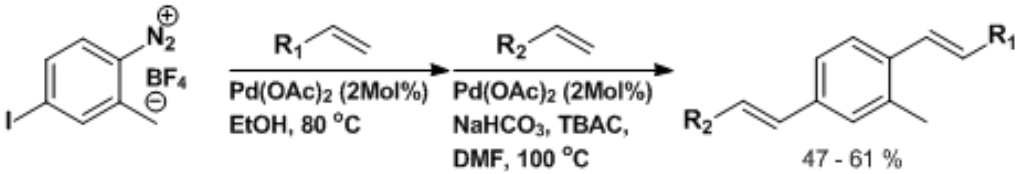
F. Akiyama, H. Miyazaki, K. Kaneda, S. Teranishi, Y. Fujiwara, M. Abe, H. Taniguchi, *J. Org. Chem.* **1980**, *45*, 2359.

Reaction in water



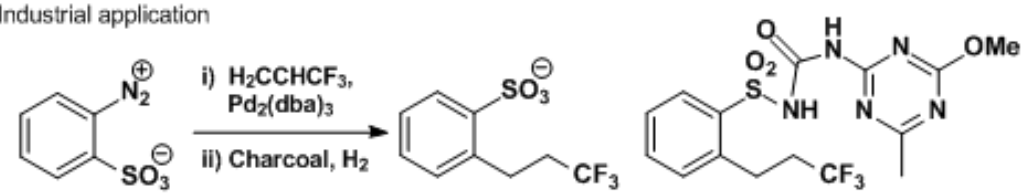
S. Sengupta, S. Bhattacharyya, *J. Chem. Soc. Perkin Trans. 1* **1993**, 1943.

Chemoselective reaction



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

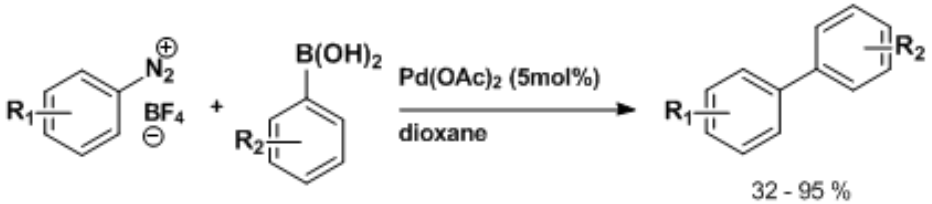
Industrial application



Prosulfron (herbizide)

VIII.2. Suzuki coupling

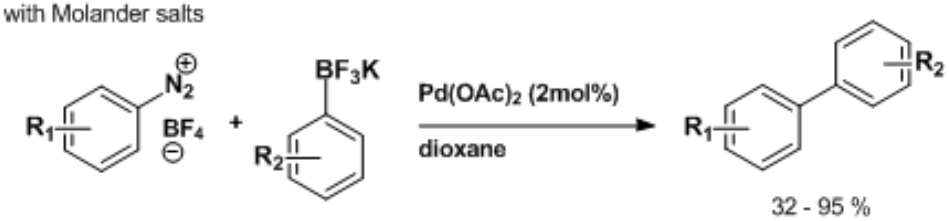
with boronic acids



R_1 = Me, Br, PhCO, OMe, COOEt, CN, NO_2, OTf
R_2 = F, Cl, OMe, Ar, naphthyl

S. 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. Battacharyya, *J. Org. Chem.* **1997**, *62*, 3405; S. Sengupta, S. K. Sadhukhan, *Tet. Lett.* **1998**, *39*, 715.

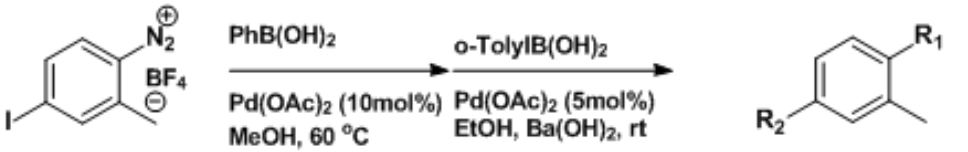
with Molander salts



R_1 = Me, PhCO, OMe, COOEt, NO_2, Br, F, I, OTf
R_2 = F, Cl, OMe, SPh, PhCO, I, OTf, naphthyl

S. 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

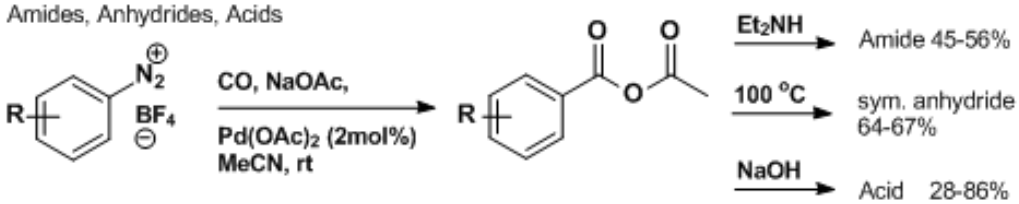


R_1 = Ph, R_2 = o-Tol
40 %

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

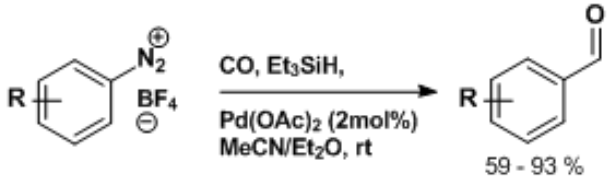
VIII.3. Carbonylative coupling

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. Nigira, F. Wada, T. Matsuda, *J. Org. Chem.* **1981**, *46*, 4413.

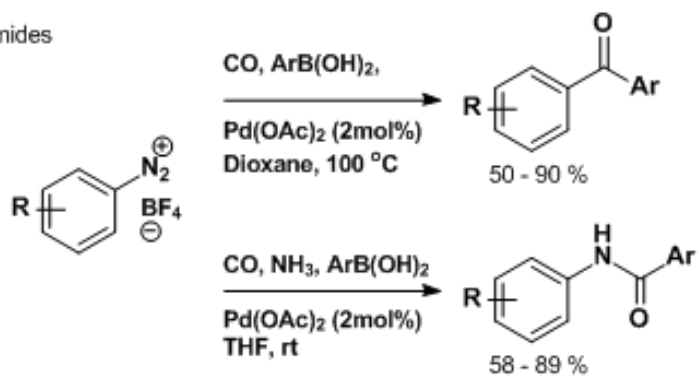
Aldehydes



R = Me, Ph, Cl, Br, COMe, COOEt, OMe, I, NO_2

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

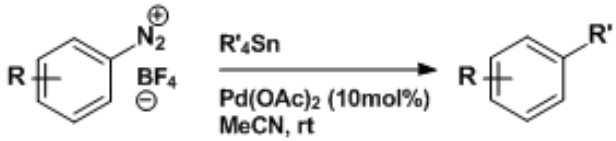
Ketones, Amides



R = Me, tBu, Br, NO_2, Ar, naphthyl
Substituents on Ar: me, OMe, Ar, CH=CHPh

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

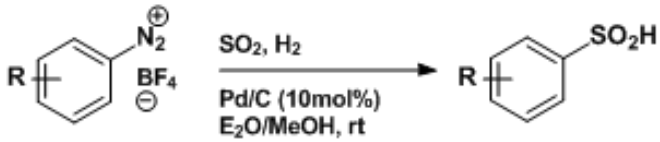


R = Me, Cl, Br, NO_2
H
Me

R' = Me 34 - 95 %
vinyl 80 %
Ph 66 %

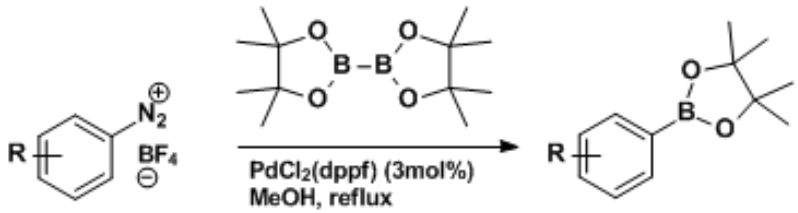
K. Kikukawa, K. Kono, F. Wada, T. Matsuda, *J. Org. Chem.* **1983**, *48*, 1333.

VIII.5. Heteroatom coupling



R = Me, Cl, Br, NO_2 81 - 93 %

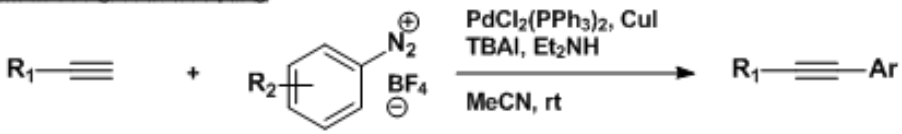
K. Kikukawa, T. Totoli, F. Wada, T. Matsuda, *J. Organomet. Chem.* **1984**, *270*, 283; L. S. Varnedoe, B. D. Angel, J. L. McClellan, J. M. Hanna Jr., *Lett. Org. Chem.* **2010**, *7*, 1



R = Br, Me, I COOMe, OMe, NO_2, Ar 42 - 91 %

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

VIII.6. Sonogashira coupling



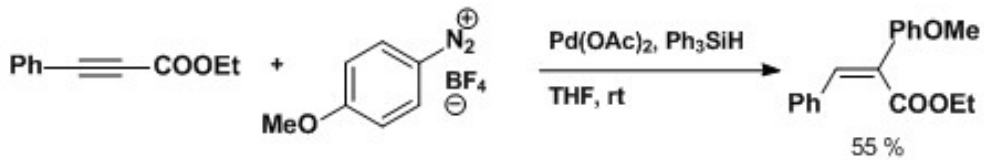
R_1 = alkyl, CH_2OH, $SiMe_3$, pyridine, aniline, Ar
R_2 = OMe, Cl, MeCO, Br, CN, CF_3, NO_2

63 - 92 %

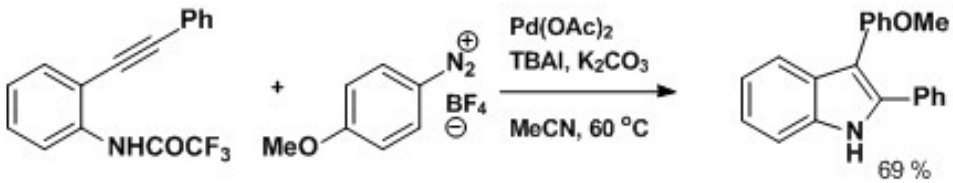
G. Fabrizi, A. Goggiamani, A. Sferrazza, S. Cacchi, *Angew. Int. Ed.* **2010**, *49*, 4067.

T. Brueckl

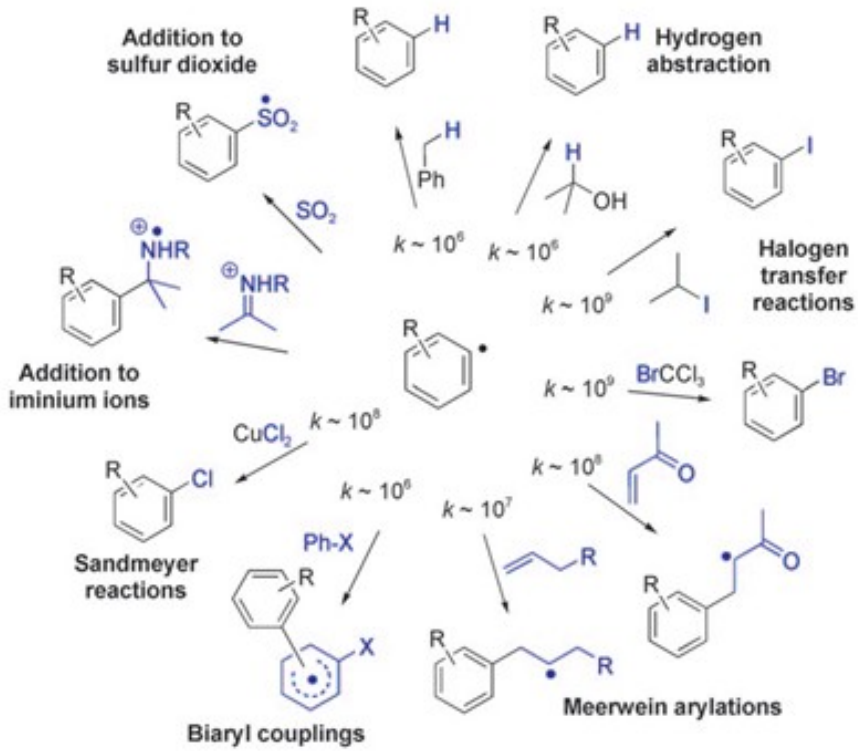
Aryldiazonium Chemistry



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.