Table 1. Magnetic susceptibility of pyrolyzed PAN and PHDD

Sample	Carbon yield (%)	$\chi_g \times 10^6$ (emu/g) (measured)	$\chi_g \times 10^6$ (emu/g) (corrected)
PAN-A	54	0.48	0.96
PAN-B	54	−0.23	0.27
HDD	−	−0.97	−0.47
PHDD	22	−0.29	0.21

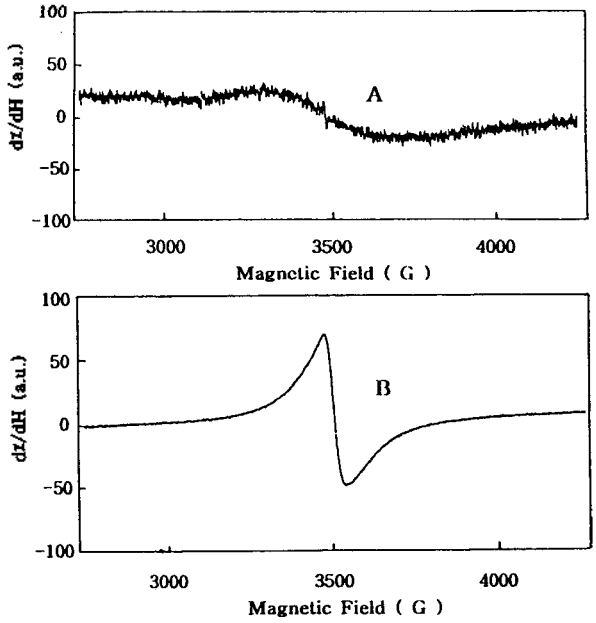

Figure 3. ESR spectra of PHDD (A) and PAN-A (B).

obtained from 9.745 GHz X-band was shown in Figure 3. Although the signal has a large fluctuation because of the conductivity of carbon powder, the calculated g-value was to confirm the presence of carbon radicals. Ovchinnikov reported that ferromagnetic carbon was obtained by pyrolysis of PAN and magnetic separation with poor reproducibility.[5] The comparative data in Table 1 suggest the possibility of forming ferromagnetic carbon by pyrolysis of PHDD. More detailed and controlled pyrolysis remained unsolved.

Acknowledgment. This research is a part of works supported by research fund for advanced materials (1993), Ministry of Education. ESR spectra are debt to Korea Basic Science Institute.

References

1. (a) Miller, J. S.; Dougherty, D. A. *Angew. Chem. Adv. Mater.* **1989**, *101*, 985. (b) Allinson, A.; Bushby, R. J.; Paillaud, J.-L. *J. Mater. Sci. Mater. Elec.* **1994**, *67*. (c) Miller, J. S. *Adv. Mater.* **1994**, *6*, 322. (d) Chang, W. G. *Chemworld(Korea)*, **1995**, *35*, 39. (d) Dulog, L. *Nachr. Chem. Tech. Lab.* **1990**, *38*, 445.
2. (a) Torrance, J. B.; Bagus, P. S.; Johannsen, I., Nazzal, A. I.; Parkin, S. S. P.; Batail, P. *J. Appl. Phys.* **1988**, *63*, 2962. (b) Yamaguchi, K.; Toyada, Y.; Fueno, T. *Kagaku(Japan)*, **1986**, *41*, 585.
3. (a) Izuoka, A.; Murata, S.; Sugawara, T.; Iwamura, H. *J. Am. Chem. Soc.* **1987**, *109*, 2631. (b) Miller, J. S.; Epstein, A. J.; Reiff, W. M. *Chem. Rev.* **1988**, *88*, 201. (c) Rajca, A. *Adv. Mater.* **1994**, *6*, 605.
4. (a) Ovchinnikov, A. A.; Spektor, V. N. *Synthetic Metals* **1988**, *27*, B615. (b) Miura, Y.; Ushitani, Y.; Inui, K.; Teki, Y.; Takui, T.; Itoh, K. *Macromol.* **1993**, *26*, 3698. (c) Fujii, A.; Ishida, T.; Koga, N.; Iwamura, H. *Macromol.* **1991**, *24*, 1077. (d) Teki, Y.; Takui, T.; Itoh, K.; Iwamura, H.; Kobayashi, K. *J. Am. Chem. Soc.* **1986**, *108*, 2147. (e) Tprrance, J. B.; Odstra, S.; Nazzal, A. *Synthetic Metals* **1987**, *19*, 709.
5. (a) Ovchinnikov, A. A.; Abdurakhmanov, U.; Kuznetsov, A. A.; Magrupov, M. A.; Spektor, A. A. *Dokl. Akad. Nauk. SSSR* **1988**, *302*, 885. (b) Ovchinnikov, A. A.; Shamovsky, I. L. *J. Mol. Str.* **1991**, *251*, 133.
6. Armitage, J. B.; Cook, C. L.; Entwistle, N.; Jones, E. R. H.; Whiting, M. C. *J. Chem. Soc.* **1947**, 1998.
7. (a) Wegner, G. *Polym. Lett.* **1971**, *9*, 133. (b) Wegner, G. *Z. Naturforschg.* **1969**, *24b*, 824.
8. Jenkins, G. M.; Kawamura, K. *Polymeric carbons-carbon fibers, glass and char*; Cambridge University Press: London, U. K., 1976; p 14.
9. Carlin, R. L. *Magnetochemistry*; Springer-Verlag: Heidelberg, Germany, 1986; p 4.

1,2,4-Triazine(VI): Synthesis of 6-Ethynyl-1,2,4-triazines from 6-Bromo-1,2,4-triazines through Pd-Catalyzed Coupling Reaction

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Received July 9, 1996

Palladium-catalyzed cross-coupling reaction of heteroaryl halides with monosubstituted olefines and acetylenes are useful for the alkenylation and alkynylation of heteroaromatic rings. Heck[1] and Sonogashira[2] reported that iodobenzene was readily coupled with monosubstituted acetylenes in the presence of catalytic amount of bis(triphenylphosphine)palladium dichloride-cuprous iodide to afford 1-substituted 2-phenylacetylenes. It is conveniently applied to the synthesis of pyridine,[3] pyrimidine,[4] pyrazine,[5] pyridazine,[6] quinazoline[7] and pterin[8] derivatives from corresponding heteroaryl halides.

Nevertheless, there are only a few works on the preparation of 1,2,4-triazine derivatives with an acetylenic side chain by palladium-catalyzed cross-coupling reaction of 1,2,4-triazine halides with monosubstituted acetylenes. Konno[9] reported that 3-iodo-1,2,4-triazines and 5-iodo-1,2,4-triazines were reacted with mono-substituted acetylene to give 3-acetylenyl-1,2,4-triazines and 5-acetylenyl-1,2,4-triazines, which were hydrated to 3-acetyl-1,2,4-triazines and 5-acetyl-1,2,4-triazines respectively. Neunhoeffer[10] reported that 6-iodo-5-methoxy-1,2,4-triazine, which was synthesized through the iodination of 6-lithio-5-methoxy-1,2,4-triazine, was reacted well with (trimethylsilyl)acetylene to give 6-(trimethylsilyl)ethynyl-1,2,4-triazine. However, there is difficulty to synthesize various 6-iodo-1,2,4-triazines through the 6-lithio-1,2,4-triazines since 5-methoxy is required to them. But it is possible to synthesize various 6-bromo-1,2,4-triazines when electron donating groups, such as amino, and N,N-dimethyl amino group are at 3-position of 1,2,4-triazine ring.[11,12] The various 6-bromo-1,2,4-triazines could be used to synthesize various 6-ethynyl-1,2,4-triazines by the palladium-catalyzed coupling reaction with monosubstituted acetylenes. If the transformation of the acetylene group to the saturated ethyl by the reduction is possible, 6-ethynyl-1,2,4-triazines could be used to synthesize various 6-alkyl-1,2,4-triazines. Also, if the transformation of the acetylene group to 1,2-dicarbonyl compounds by the oxidation is possible, which are very important intermediate to synthesize 1,2,4-triazine ring, they could be used to synthesize 6,5′- and/or 6,6′-Bis-1,2,4-triazinyls.

Thus, we report in this paper the synthesis of 6-ethynyl-1,2,4-triazines by the palladium-catalyzed coupling reaction. We also report one of the results of their reduction to 6-alkyl-1,2,4-triazine and oxidation to 6-ethanedionyl-1,2,4-triazine.

The coupling reaction of 6-bromo-3-N,N-dimethylamino-1,2,4-triazine (**1a**)[11,12] with phenylacetylene (**2f**) was carried out in the presence of catalytic amount of bis(triphenylphosphine)palladium dichloride[13]-cuprous iodide and triethylamine in acetonitrile at 80 ℃ to give 3-N,N-dimethylamino-6-phenylethynyl-1,2,4-triazine (**3h**) in 66% yield (Scheme 1).

Similarly, the coupling reaction of 6-bromo-3-N,N-dimethylamino-1,2,4-triazine (**1a**) with N-methyl-N-propagylaniline (**2g**) was also successfully achieved under the same reaction conditions with 47% yield of 3-N,N-dimethylamino-6-(N-methyl-N-phenylamino)propynyl-1,2,4-triazine (**3i**). 6-Bromo-3-N,N-dimethylamino-5-hydroxy-1,2,4-triazine (**1b**),[11,14] and 6-bromo-3,5-diamino-1,2,4-triazine (**1c**),[11,15] were coupled with phenylacetylene (**2f**) with reduced yields. 3-Amino-6-bromo-5-hydroxy-1,2,4-triazine (**1d**)[16,17] was also successfully reacted with both phenylacetylene (**2f**) and N-methyl-N-propagylaniline (**2g**) under the same reaction conditions to give 3-amino-5-hydroxy-6-phenylethynyl-1,2,4-triazine (**3l**) and 3-amino-5-hydroxy-6-(N-methyl-N-phenylamino)propynyl-1,2,4-triazine (**3m**) with much reduced yields (Scheme 1). Also 3-amino-6-bromo-1,2,4-triazine N_2-oxide (**1e**)[18,19] were successfully coupled with phenylacetylene (**2f**) with much reduced yields (Scheme 2). Most of the remainings were the unidentifiable dark brown oil, which were hardly moved in silica gel column. All effort to increase the yields, such as changing solvents, reaction temperature and reaction time, did not work at all. At this moment we don't know the proper reason why the yields are so much reduced.

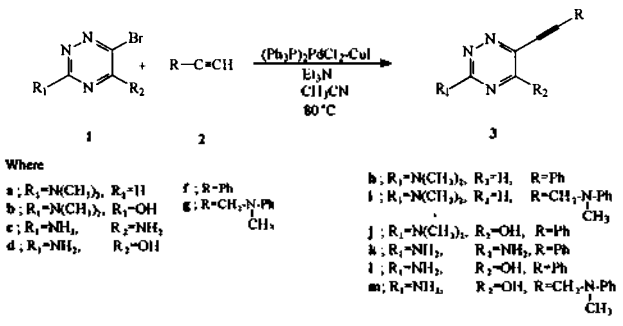
Even though the yields were greatly reduced, the reason we chose those compounds was that amino and hydroxy are believed to be necessary to make biologically active compounds and used as the important intermediates to synthesize potential antifolates.[20]

The reduction of 3-N,N-dimethylamino-6-phenylethynyl-1,2,4-triazine (**3h**) was carried out successfully with both Pd/C and $Pt(OH)_2$ catalyst to give 3-N,N-dimethyamino-6-phenylethyl-1,2,4-triazine (**4**)[21,22] with 71% yield (Scheme 3). This would be another route to get various 6-substituted-1,2,4-triazines. Otherwise, the most common route to obtain 6-substituted-1,2,4-triazine derivatives is to condense various pyruvonitriles or pyruvic acids with aminoguanidine and/or semicarbarzide.[23,24]

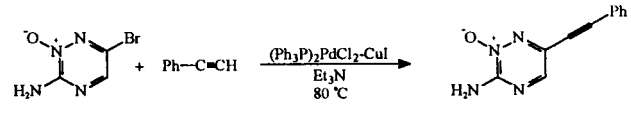
Also the oxidation[25] of 6-ethynyl group to 1,2-dicarbonyl with $KMnO_4$(aq) was carried out and gave good results (Scheme 3). This is the first observation to get 1,2,4-triazines with 1,2-dicarbonyl group at 6-position, and these compound could be used to synthesize 6,5′- and/or 6,6′-Bis-1,2,4-triazinyls, which might be the new potential ligands for various transition metals.[26]

All the products were identified by their NMR and mass spectral data.

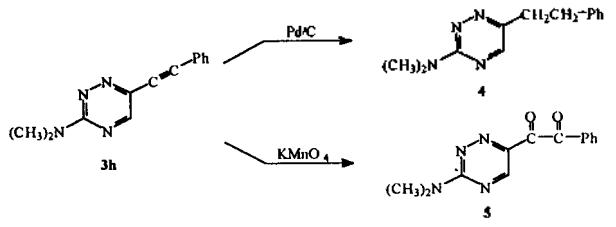
The conclusion is that 6-ethynyl-1,2,4-triazines were successfully synthesized by the Pd catalyzed coupling reaction from 6-bromo-1,2,4-triazines and could be used as the good intermediates for the synthesis of 1,2,4-triazines with alkyl and 1,2-dicarbonyl group at 6-position.



Scheme 1.



Scheme 2.



Scheme 3.

Experimental

Bis(triphenylphosphine)palladium dichloride [$Pd(PPh_3)_2Cl_2$] was prepared according to the method by Heck. The following 6-bromo-1,2,4-triazines were prepared by the known methods: 6-bromo-3-N,N-dimethylamino-1,2,4-triazine (**1a**), 6-bromo-3-N,N-dimethylamino-5-hydroxy-1,2,4-triazine (**1b**), 6-bromo-3,5-diamino-1,2,4-triazine (**1c**), 3-amino-6-bromo-5-hydroxy-1,2,4-triazine (**1d**), 3-amino-6-bromo-1,2,4-triazine N_2-oxide (**1e**).

NMR and mass spectra were recorded on Varian EM-360, General Electric QE-300 and Shimazu GC MS-QP-1000A, respectively. Melting points were determined on a Electrothermal melting point apparatus and are uncorrected.

3-N,N-Dimethylamino-6-phenylethynyl-1,2,4-triazine (3h). (general method)

6-Bromo-3-N,N-dimethylamino-1,2,4-triazine (**1a**) (0.6 g, 3.0 mmol), $Pd(PPh_3)_2Cl_2$ (0.12 g) and CuI (0.032 g) were dissolved in acetonitrile (15 mL) with phenylacetylene (0.4 mL, 3.6 mmol) and triethylamine (2.1 mL, 15 mmol). After the mixture was refluxed for 6 hrs, the reaction mixture was concentrated to the dryness under reduced pressure. A proper quantity of water was added to the residue and extracted with chloroform. The chloroform solution was dried with $MgSO_4$ and evaporated to dryness after filtering the $MgSO_4$. The product was purified by silica gel column chromatography using ethyl acetate and pet. ether (1 : 5) as an eluent. Yield: 66%, mp 152-154 ℃; ^1H NMR ($CDCl_3$) δ 8.25 (s, 1H, C_5-H), 7.25-7.75 (m, 5H, Ph), 3.32 (s, 6H, $N(CH_3)_2$); MS: m/e (relative intensity) 224 (M^+, 10), 126 (100).

3-N,N-Dimethylamino-6-(N-methyl-N-phenylamino) propynyl-1,2,4-triazine (3i). 6-Bromo-3-N,N-dimethylamino-1,2,4-triazine (**1a**) (0.3 g, 1.5 mmol), $Pd(PPh_3)_2Cl_2$ (0.06 g) and CuI (0.024 g) were dissolved in acetonitrile (7.5 mL) with N-methyl-N-propagylaniline (0.232 g, 1.6 mmol) and triethylamine (1.1 mL, 7.5 mmol). After the mixture was refluxed for 6 hrs, the reaction mixture was treated like the above general method to give **3i**. Yield: 47%, mp 104-106 ℃; ^1H NMR ($CDCl_3$) δ 8.05 (s, 1H, C_5-H), 6.80-7.50 (m, 5H, Ph), 4.32 (s, 2H, CH_2), 3.26 (s, 6H, $N(CH_3)_2$), 3.04 (s, 3H, CH_3); MS: m/e (relative intensity) 267 (M^+, 67), 162 (100).

3-N,N-Dimethylamino-5-hydroxy-6-phenylethynyl-1, 2,4-triazine (3j). 6-Bromo-3-N,N-dimethylamino-5-hydroxy-1,2,4-triazine (**1b**) (0.3 g, 1.38 mmol), and phenyl-acetylene (0.18 mL, 1.62 mmol) were dissolved in triethylamine (12 mL) with $Pd(PPh_3)_2Cl_2$ (0.052 g) and CuI (0.014 g). After the mixture was stirred for 24 hrs in nitrogen atmosphere at room temperature, the reaction mixture was treated like the above general method to give **3j**. Yield: 37%, mp 200-202 ℃; ^1H NMR ($CDCl_3$) δ 7.45-7.87 (m, 5H, Ph), 7.21 (s, 1H, C_5-H), 3.35 (s, 6H, $N(CH_3)_2$); MS: m/e (relative intensity) 240 (M^+, 29), 212 (18.9), 196 (5.1), 169 (9.5), 141 (13.2), 127 (6.8).

3,5-Diamino-6-phenylethynyl-1,2,4-triazine (3k). A mixture of 6-bromo-3,5-diamino-1,2,4-triazine (**1c**) (0.2 g, 1.5 mmol), $Pd(PPh_3)_2Cl_2$ (0.060 g), CuI (0.016 g), phenylacetylene (0.2 mL, 1.8 mmol) and triethylamine (1 mL) in DMF (7 mL) was stirred for 24 hrs at room temperature. The reaction mixture was treated like the above general method to give **3k**. Yield: 10%, mp 210-212 ℃; ^1H NMR (DMSO-d_6) δ 7.42-7.69 (m, 5H, Ph), 6.76 (broad, NH_2); MS: m/e (relative intensity) 211 (M^+, 79), 169 (11.9), 155 (27.7), 141 (100).

3-Amino-5-hydroxy-6-phenylethynyl-1,2,4-triazine (3l). A mixture of 3-amino-6-bromo-5-hydroxy-1,2,4-triazine (**1d**) (0.3 g, 1.58 mmol), $Pd(PPh_3)_2Cl_2$ (0.060 g), CuI (0.016 g), phenylacetylene (0.2 mL, 1.8 mmol) and triethylamine (1 mL) in DMF (10 mL) was warmed at 70 ℃ for 3 hrs. The reaction mixture was worked up like the general method to give **3l**. Yield: 28%, mp >300 ℃; ^1H NMR (DMSO-d_6) δ 7.96-7.36 (m, 5H, Ph), 7.78 (s, 1H, C_5-H), 7.36 (s, 2H, NH_2); MS: m/e (relative intensity) 212 (M^+, 100), 184 (21.5), 156 (15.2), 141 (5.2), 113 (19.6).

3-Amino-5-hydroxy-6-(N-methyl-N-phenylamino) propynyl-1,2,4-triazine (3m). 3-Amino-6-bromo-5-hydroxy-1,2,4-triazine (**1d**) (0.1 g, 0.52 mmol), $Pd(PPh_3)_2Cl_2$ (0.024 g) and CuI (0.0084 g) were dissolved in DMF (3.4 mL) with N-methyl-N-propagylaniline (0.078 g, 0.125 mmol) and triethylamine (0.37 mL, 2.5 mmol). After the mixture was stirred for 4.5 hrs at 110 ℃, the reaction mixture was worked up like the above general method to give **3m**. Yield: 10%, mp 180 ℃ (decomp.); ^1H NMR ($CDCl_3$) δ 6.74-7.28 (m, 5H, Ph), 5.37 (s, 2H, NH_2), 4.61 (d, 2H, CH_2), 3.11 (s, 3H, CH_3); MS: m/e (relative intensity) 255 (M^+, 48).

3-Amino-6-phenylethynyl-1,2,4-triazine N_2-Oxide (3 n). A mixture of 3-amino-6-bromo-1,2,4-triazine N_2-oxide (**1 e**) (0.3 g, 1.58 mmol), $Pd(PPh_3)_2Cl_2$ (0.028 g), CuI (0.008 g), phenylacetylene (0.2 mL, 1.8 mmol) and triethylamine (12 mL) was stirred for 24 hrs in nitrogen atmosphere at room temperature. The reaction mixture was worked up like the general method to give **3n**. Yield: 12%, mp 188-190 ℃; ^1H NMR ($CDCl_3$) δ 7.91 (s, 1H, C_5-H), 7.35-7.58 (m, 5H, Ph), 6.32 (s, 2H, NH_2); MS: m/e (relative intensity) 212 (M^+, 24), 196 (12.9), 184 (14.2), 182 (71.1), 140 (100), 125 (77.7), 113 (31.4).

3-N,N-Dimethylamino-6-phenylethyl-1,2,4-triazine (4). A mixture of 3-N,N-dimethylamino-6-phenylethynyl-1,2, 4-triazine (**3h**) (0.3 g, 1.34 mmol) and 10% palladium-on-charcoal (0.334 g) in 50 mL of ethyl acetate was hydrogenated in autoclave at 2 atm at room temperature for 24 hrs. The reaction mixture was diluted with ethyl alcohol and filtered. The solvent was removed under reduced pressure, and the product was purified by silica gel column chromatography using ethyl acetate and *n*-hexane (1 : 2) as an eluent. Yield: 71%, mp 34-36 ℃; ^1H NMR ($CDCl_3$) δ 7.77 (s, 1H, C_5-H), 7.10-7.23 (m, 5H, Ph), 3.17 (s, 6H, $N(CH_3)_2$), 2.94-4.05 (m, 4H, CH_2CH_2); MS: m/e (relative intensity) 228 (M^+, 21), 130 (6.7), 91 (100).

3-N,N-Dimethylamino-6-phenylethandionyl-1,2,4-triazine (5). 3-N,N-Dimethylamino-6-phenylethynyl-1,2,4-triazine (**3h**) (0.3 g, 1.34 mmol) was dissolved in acetone (52 mL) at room temperature. The solution of $NaHCO_3$ (0.07 g) and $MgSO_4$ (0.7 g) in water (30 mL) was added while magnetically stirring, and then the powdered $KMnO_4$ (0.4 g, 2.5 mmol) was added to it in one portion. After stirring for additional 2 hrs, manganese dioxide was precipitated when the solution of $NaNO_2$ (0.35 g) in 3.5 mL for 10% H_2SO_4 was added slowly in small portions. The precipitate was filtered and the solution was extracted with the mixture of *n*-hexane and ethyl acetate (1 : 1). The organic layer was separated and the solvent was evaporated to dryness. The reaction mixture was dissolved in ether and the ether solution was washed with 5% NaOH (4×25 mL) and saturated NaCl

solution. The ether solution was dried with anhydrous $MgSO_4$ and evaporated to dryness under rotary rvaporator. The product was purified by silica gel column chromatography using ethyl acetate and pet. ether (1 : 3) as an eluent. Yield: 29%, mp 99-101 ℃; ^1H NMR ($CDCl_3$) δ 8.86 (s, 1H, C_5-H), 7.47-7.96 (m, 5H, Ph), 3.32-3.47 (d, 6H, $N(CH_3)_2$); MS: m/e (relative intensity) 256 (M^+, 28), 151 (25.6), 123 (42.2), 105 (100).

Acknowledgment. This work was supported by the Basic Science Research Institute Program (BSRI-95-3402), Ministry of Education.

References

1. Heck, R. F.; Nolley, Jr. J. P. *J. Org. Chem.* **1972**, *37*, 2320.
2. Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, *16*, 4467.
3. Sakamoto, T.; Shiraiwa, M.; Kondo, Y.; Yamanaka, H. *Synthesis.* **1983**, 312.
4. Edo, K.; Sakamoto, T.; Yamanaka, H. *Chem. Pharm. Bull.* **1978**, *26*, 3843.
5. Akita, Y.; Kanekawa, H.; Kawasaki, T.; Shiratori, I.; Ohta, A. *J. Heterocyclic Chem.* **1988**, *25*, 975.
6. Ohsawa, A.; Abe, Y.; Igeta, H. *Chem. Pharm. Bull.* **1980**, *28*, 3488.
7. Jones, T. R.; Thornton, T. J.; Flinn, A.; Jackman, A. L.; Newell, D. R.; Calvert, A. H. *J. Med. Chem.* **1989**, *32*, 847.
8. Taylor, E. C.; Ray, P. S. *J. Org. Chem.* **1987**, *52*, 3997.
9. Konno, S.; Fujimura, S.; Yamanaka, H. *Heterocycles* **1984**, *22*, 2245.
10. Ple, N.; Turck, A.; Queguiner, G.; Glassl, B.; Neunhoeffer, H. *Liebigs Ann. Chem.* **1993**, 583.
11. Chang, P. K. *J. Org. Chem.* **1961**, *26*, 1118.
12. Keen, B. T.; Radel, R. J.; Paudler, W. W. *J. Org. Chem.* **1977**, *42*, 3498.
13. Heck, R. F. *Palladium Reagents in Organic Syntheses*; Academic Press: London, U. K., 1985; p 18.
14. Fusco, R.; Rossi, S. *Tetrahedron* **1958**, *3*, 209.
15. Rykowski, A. *Synthesis* **1985**, 884.
16. Sasaki, T.; Minamoto, K. *Chem. Pharm. Bull.* **1964**, *12*, 1329.
17. Lovelette, C. A. *J. Heterocyclic Chem.* **1979**, *16*, 555.
18. Radel, R. J.; Keen, B. T.; Wong, C.; Paudler, W. W. *J. Org. Chem.* **1977**, *42*, 546.
19. Radel, R. J.; Atwood, J. L.; Paudler, W. W. *J. Org. Chem.* **1978**, *43*, 2514.
20. Blaney, J. M.; Hansch, C.; Silipo, C.; Vittoria, A. *Chem. Rev.* **1983**, *84*, 333.
21. Taylor, E. C.; Wong, G. S. K. *J. Org. Chem.* **1989**, *54*, 3618.
22. Taylor, E. C.; Wendy, B. Y.; Spanka, C. *J. Org. Chem.* **1996**, *61*, 1261.
23. Paudler, W. W.; Chen, T. K. *J. Heterocyclic Chem.* **1970**, *7*, 767.
24. Wasti, K.; Joullie, M. M. *J. Chem. Soc., Perkin I*, **1976**, 2521.
25. Lee, D. G.; Chang, V. S. *Synthesis* **1978**, 462.
26. We will report later about the new ligand experimental results.

Hydrosilylation of Carbonyls and Alkenes with Alkylsilanes Catalyzed by Activated Metals

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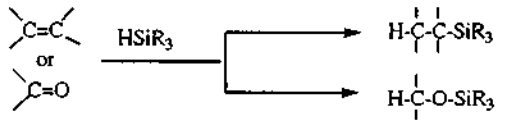
Received August 1, 1996

The application of activated metals (M*) to catalysis is an interesting and challenging subject in view of their unique reactivites, which have been extensively reported in the last decade.[1] Recently we reported the first successful utilization of activated nickel powder prepared from the reaction of NiI_2 with Li as a catalyst in hydrosilylation of alkenes with chlorosilane.[2]



(1)

However, hydrosilylation (1) on carbonyls-alkylsilane and alkene-alkylsilane with this activated nickel powders was not investigated. In continuation of our work, we have examined a broad range of activated metals that encompasses Zr*, Mo*, Ni* for hydrosilylation reaction. We describe here the hydrosilylation of carbonyl compounds and alkenes with alkylsilanes catalyzed by activated metals prepared from this methods. Results are summerized at Table 1. The use of precious metals (Pt[3], Pd[4], Rh[5]) can be circumvented by using a highly reactive metal powders as a catalyst for hydrosilylation. The highly activated metal powders such as Zr*, Mo*, Ni* are readily prepared by the reaction of the corresponding anhydrous metal halides (Cl, Br, I) with equivalent of metals (Li, Na, Cd, Mg, Zn) in freshly distilled tetrahydrofuran (THF) or dimethoxyethane (DME). After refluxing these mixture under nitrogen atmosphere for 1 hr and cooling to room temperature, the finely divided metal appeared as black powders which settled down in a dark solution (in most cases). The activated metal in solution was used in this investigation without any further treatment. The silanes and substrates (catalyst : silanes : substrates = 1 : 2.5 : 2; molar ratio) were added to freshly prepared highly reactive metal solution and refluxed under nitrogen for 3-18 h. The resulting solution was then allowed to cool to room temperature and hexane was added to become a clear solution along with settled down the catalyst. Product isolation was straightforward. The solution was filtered to remove the catalyst through a pad of silica gel or filter paper using hexane-methylene chloride solvent as an eluent. Removal of the solvent under reduced pressure gave the corresponding hydrosilylating products. The reaction proceeded smoothly and without vigorous exothermic reaction in most cases. The final product mixture was free of polymer, containing only the unreacted reagents and the desired hydrosilylated product. Interestingly, commercially available metal powders such as nickel,