Tetrahedron Letters,Vol.29,No.5,pp 545-546,1988 0040-4039/88 $3.00 + .00
Printed in Great Britain Pergamon Journals Ltd.

ACTIVATION OF REDUCING AGENTS. SODIUM HYDRIDE CONTAINING COMPLEX REDUCING AGENTS 25. A ONE POT ONE REAGENT CROSS-COUPLING REACTION OF ARYL HALIDES

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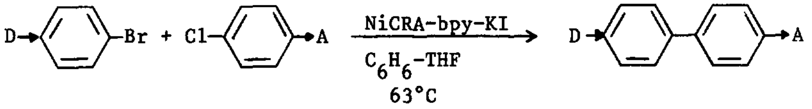
Abstract : The preparation of NiCRA [NaH-$\overset{t}{\text{Am}}$ONa-Ni(OAc)$_2$] in the presence of 2,2'-bipyridyl and KI leads to a reagent (termed NiCRA-bpy-KI) which is shown to be one of the most efficient Ni containing reagents reported so far for the cross-coupling of aryl halides.

Liganded Reducing Agents (CRAL) of the type NaH-RONa-MX$_n$-Ligand, where MX$_n$ is a metal salt and the ligand Ph$_3$P or 2,2'-bipyridyl, are useful coupling agents of aryl or vinyl halides[1], including chlorides[2,3] which are not easily coupled by other methods.[4,5] We now show that the reagent NaH/$\overset{t}{\text{Am}}$ONa/Ni(OAc)$_2$/2,2'-bipyridyl/KI, abbreviated NiCRA-bpy-KI, in the molar ratio 4/2/1/2/1 permits the one pot cross-coupling of an aryl bromide ArBr where Ar is an aryl group substituted with an electron donating group D, and an aryl chloride Ar^{1}Cl, where Ar^1 carries an electron attracting group A.



D = MeO A = CF$_3$ (1 h ; 73 %) ; F (1 h ; 72 %) ; CH(OMe)$_2$ (1 h ; 68 %) ; CMe(OCH$_2$)$_2$ (1.5 h ; 62 %)
D = OH A = CN (4 h ; 70 %) ; CH(OMe)$_2$ (1.75 h ; 63 %)
D = MeS A = CF$_3$ (2.5 h ; 61 %)
D = Me$_2$N A = CF$_3$ (2 h ; 62 %) ; A = F (3 h ; 66 %)

As may be seen from these results, the selectivity in cross-coupling varies from fair to excellent. The side products of these condensations are of course symmetrically coupled products and reduced derivatives.

General procedure

$\overset{t}{\text{Am}}$OH (20 mmol) in 10 ml benzene was added dropwise at 63°C to a suspension of degreased NaH (60 mmol), Ni(OAc)$_2$ (10 mmol) and 2,2'-bipyridyl (20 mmol) in benzene (30 ml) containing 50 mmol THF as cosolvent. In benzene, the presence of 50 mmol THF is absolutely necessary : without it, the NiCRA-bpy is inactive and no coupling reaction takes place.

After 2 h stirring at 63°C, KI (10 mmol) was added to the reagent and stirring was continued 0.5 h. The reagent was then ready for use. The aryl halides (5 mmol of each) were added with 10 ml benzene. The reaction was monitored by GC analysis of small aliquots.

After completion, the excess hydride was carefully destroyed by dropwise addition of EtOH until hydrogen evolution ceased. The mixture was then acidified (100 ml HCl 10 %). After extraction into diethyl ether, drying over $MgSO_4$ and removal of solvents the products were separated by flash chromatography. They were characterized by their spectroscopic data (IR, ^{1}H, ^{13}C NMR). The microanalyses were in agreement with the purposed structures.

Acknowledgements

We gratefully thank Ms S. BECKER for her technical assistance in this work.

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(Received in France 6 November 1987)