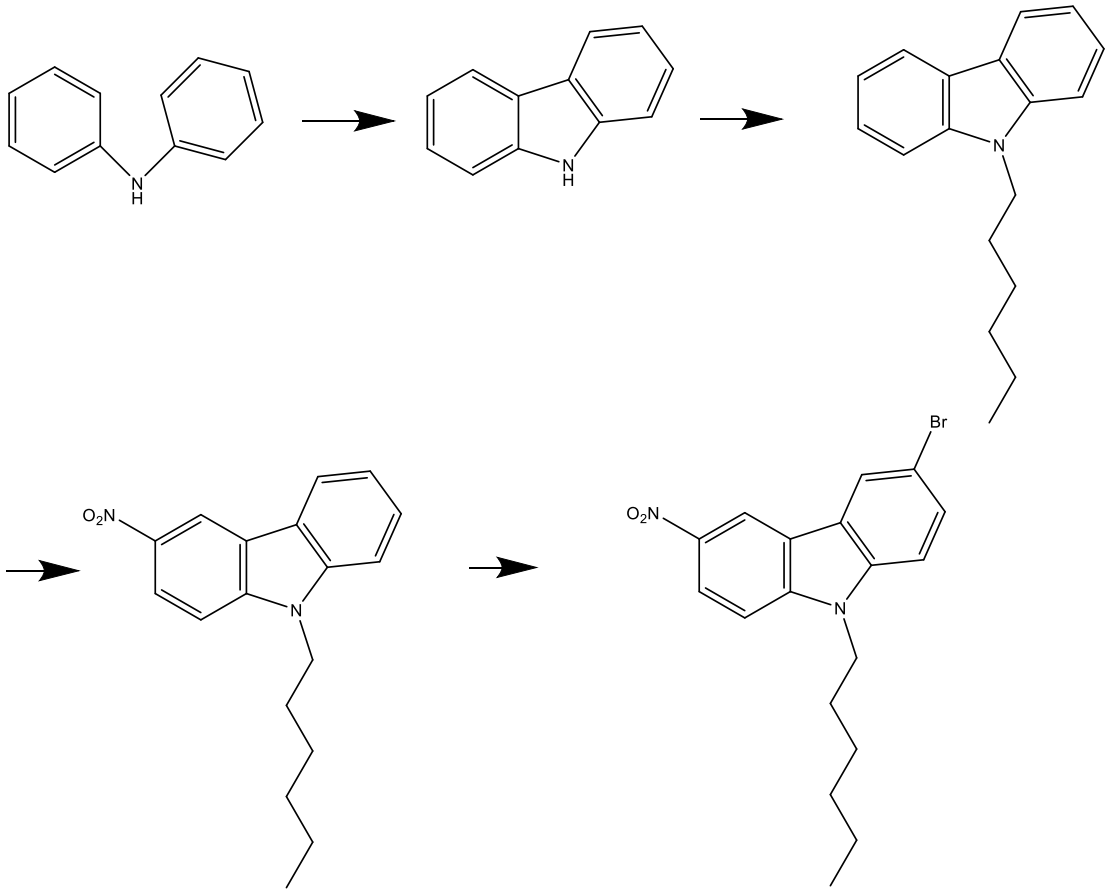
Proposal for synthesis of 9-hexyl-3-bromo-6-nitrocarbazole

Organic Chemistry lab 2



CONTENTS

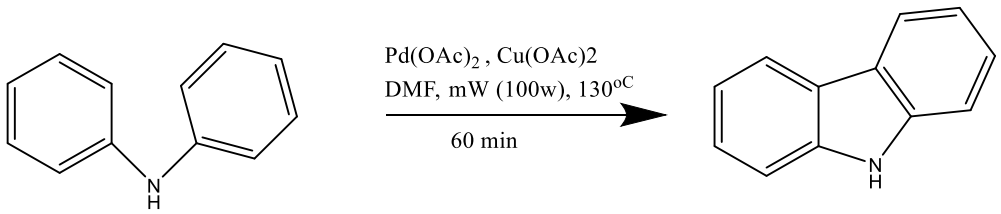
Diphenylamine
$Pd(OAc)_2$
$Cu(OAc)_2$
DMF
silica gel
petroleum ether
ethyl acetate
1 bromohexane
KOH
acetone
EtOAc
water
Hexane
1,2 dichloroethane
nitric acid
CH_2Cl_2
MgSO4

NBS
AcOEt
Na_2SO_4

MOST DANGEROUS CHEMICALS IN EVERY STEP

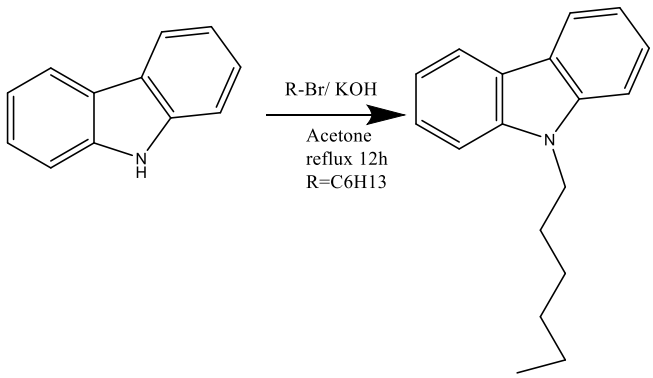
COST ACCOUNTING

Step One



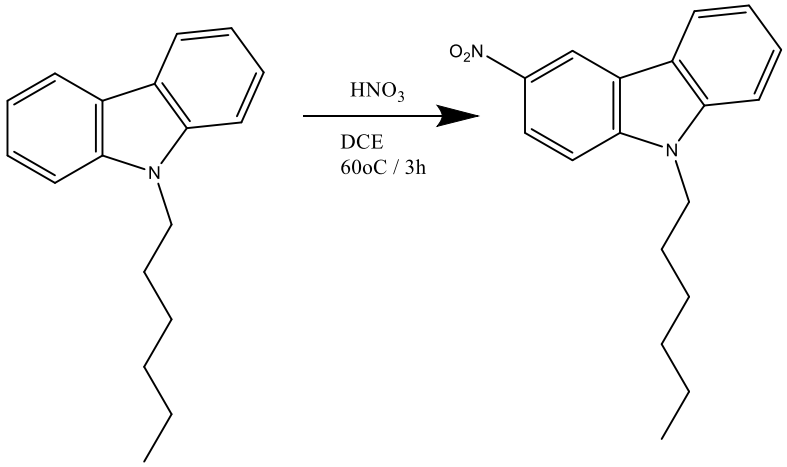
To a mixture of the suitable diarylamine, $Pd(OAc)_2$ and $Cu(OAc)_2$ was added a few drops of DMF. The mixture was introduced in a 10ml sealed tube and was irradiated at 100W and 130^{oC} for 60 min in a CEM Discover microwave reactor equipped with built-in pressure measurement sensor and a vertically focused IR sensor. After completion of the reaction, the reaction mixture was purified by flash silica gel column chromatography eluting with a petroleum ether/ethyl acetate gradient (95:5 to 90:10, v/v)

Step two



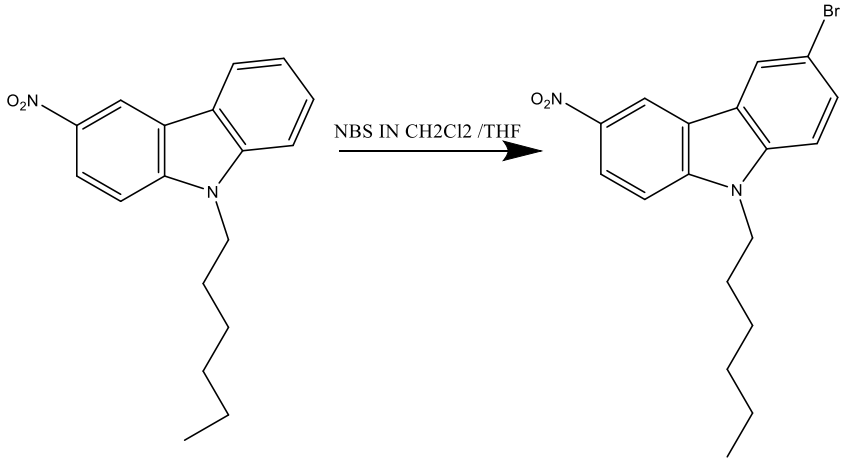
A mixture of carbazole, 1-bromohexane and KOH in acetone was heated to reflux overnight. After removing the solvent in vacuo, the mixture was extracted with EtOAc and washed with water. Column chromatography on silica gel using hexanes resulted in a clear oil.

Step three



A solution of the first compound in 1,2-dichloroethane was cooled to 0^{oC}(ice bath), to which nitric acid was added dropwise. The reaction was heated to 60^{oC} and stirred for 3h. After cooling to room temperature, water was added, and the mixture was extracted with CH_2Cl_2. The organic layer was dried with MgSO4, filtered, and solvent was removed in vacuo. The crube oil mixture was recrystallized from hexanes to give an orange solid product.

Step four



To a soln. of the 3-nitro-9H carbazole in CH_2Cl_2 containing silica gel, a soln. of NBS in CH_2Cl_2 was added dropwise. The mixture was stirred for an appropriate time in the absence of light at r.t under normal air atmosphere and GC monitoring. The mixture was then filtered, and the silica gel was with CH_2Cl_2. The combined filtrate washed with H_2O, dried with Na_2SO_4 and evaporated. The brownish solid residue was dissolved in the minimum volume of CH_2Cl_2 with soln. mixed with silica gel and evaporated and the brownish solid residue put on top of a prepared column and subjected to FC (silica gel, hexane/AcOE mixtures).

References

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