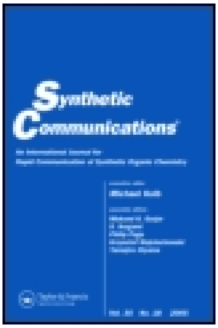

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An Improved Procedure for N-Ethynylpyrrole

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AN IMPROVED PROCEDURE FOR *N*-ETHYNYLPYRROLE

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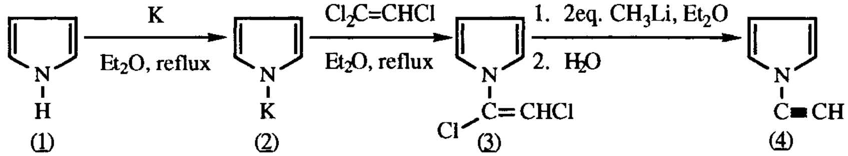
ABSTRACT

N-Ethynylpyrrole can be obtained in good overall yields by reacting pyrrole with potassium *tert*-butoxide and trichloroethene in tetrahydrofuran, and subsequently dechlorinating the adduct with methyllithium or *n*-butyllithium in diethyl ether.

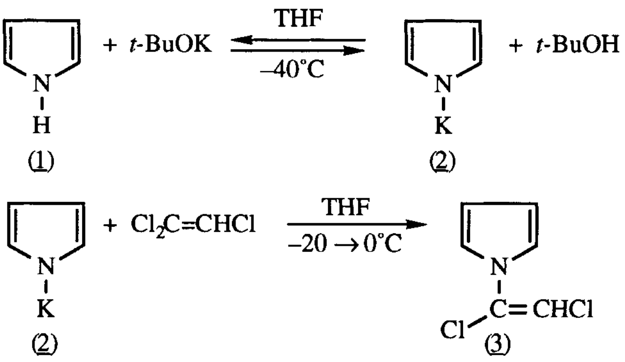
Interest in the physical properties of its derivatives has led to the first synthesis of *N*-ethynylpyrrole[1] (4):



Although the reported overall yield seems reasonable (~ 45 %), the complete conversion of potassium for the preparation of *N*-pyrrylpotassium requires prolonged heating under reflux and the use of a large excess of pyrrole. The *N*-

alkenylation of (2) is effected by refluxing a suspension of (2) in diethyl ether for several hours with a large excess of trichloroethene. Under these conditions part of the unstable (3) is converted into black, tarry material. The dechlorination of (3) carried out by the method of Ficini[2], proceeds with excellent results.

In connection with our investigations in the field of *N*-substituted pyrroles[3] we needed an efficient synthetic method for *N*-ethynylpyrrole (4). The modification we propose for the synthesis of (4) concerns the preparation of (3) from pyrrole, trichloroethene and potassium *tert*-butoxide in tetrahydrofuran. Under the relativily mild conditions of our procedure (~ -2- to 0°C) the addition of pyrrole to the(*in situ* generated dichloroacetylene is complete within 1.5 h and (3) may be obtained in yields as high as 75 %. It is not necessary to use an excess of pyrrole.



EXPERIMENTAL

1. Preparation of *N*-(1,2-dichlorovinyl)-pyrrole (3)

A 1-L, round-bottomed, three-necked flask, fitted with an efficient mechanical stirrer, a gas inlet and a thermometer-gasoutlet combination, was flushed with nitrogen. The flask was charged with freshly distilled pyrrole (0.30 mol, 20.1 g) and 220 mL of tetrahydrofuran (dried by shaking with machine-powdered KOH and subsequently distilling from $LiAlH_4$). The solution was cooled to ~ -40°C and a solution of 0.60 mol (67 g, 100 mol % excess) potassium *tert*-butoxide (commercially available, not complexed with *tert*-butyl alcohol) in 150 mL of THF was added over a short period, while keeping the temperature of the mixture below -30°C. Subsequently trichloroethene (0.30 mol, 39 g) was added in a number of portions over 15 min, at a temperature between -40 and -30°C. The temperature of the somewhat gelatinous reaction mixture (a small amount of diethyl ether may be added in order to facilate stirring) was allowed to rise to between –20 and –15°C. Stirring at this temperature was continued for 30 min, then an additional amount of trichloroethene (0.30 mol, 39 g) was added at –20°C, and the temperature of the brown mixture was allowed to rise gradually (over ~40 min) to 0°C. During this period the progress of the reaction was followed by GLC. As a rule only small relative amounts of pyrrole remain present upon prolonged stirring at 0°C. Ice water (300 mL) was added with vigorous stirring. After seperation of the layers, three extracts with small amounts (30 - 40 mL) of pentane were carried out. The combined organic solutions were washed three times with a saturated aqueous solution of NaCl or NH_4Cl (50-mL portions) and subsequently dried over potassium carbonate. After addition of 10 g of *N,N*-diethylaniline (to stabilize (3)), the solvent was removed under reduced presure (bath temperature rotary evaporator ~ 35°C). Careful fractionation of the remaining dark-brown liquid through a 30-cm Widmer column gave, after a volatile fraction, mainly consisting of *tert*-$C_4H_9OC(Cl)=CHCl$, (3), b.p. 67 -70°C/15 mm Hg, n^{20}_D 1.548, in 70 - 78 % yield. The ^{1}H NMR spectrum of (3) (CCl_4, Me_4Si as internal standard) shows signals around 6.90 ppm, 6.15 ppm (multiplets) and 6.02 ppm (CH=, singlet). Compound (3) rapidly turns dark at room temperatures and should be stored at –20°C in the presence of a small amount of *N,N*-diethylaniline (~ 1 mol %).

2. Preparation of *N*-ethynylpyrrole (4) (Compare ref. 2)

To a mixture of 0.20 mol of (3) and 50 ml of dry diethyl ether was added over 30 min a solution of ~0.45 mol (slight excess) of methyllithium[4] in ~350 ml of ether. During this addition the temperature was kept between –5 and +5°C. After an additional period of 2 h at ~15°C, the solution was cooled to below –30°C and 50 mL of ice water was added over 5 min with vigorous stirring, care being taken that the temperature of the mixture did not rise above 5°C. The upper layer was dried over anhydrous $MgSO_4$, after which the greater part of the ether was distilled off under nitrogen through a 40-cm Widmer column, keeping the bath temperature below 85°C in the last stage of the distillation. After most of the ether had been distilled off, the distillation was continued under reduced pressure (water aspirator). The product was collected in a *single* receiver. This was placed in a bath at –20°C as soon as the pressure had dropped below 50 mm Hg. In order to remove small amounts of ether from the distillate, this procedure was repeated, giving pure *N*-ethynylpyrrole in ~80 % yield. A small part was redistilled (under N_2) through a short column: b.p. 108°C/ 760 mm Hg, n^{20}_D 1.513. The product turned brown at room temperature.

Commercially available available *n*-butyllithium can be used instead of methyllithium. In that case the hexane is first removed from the solution of *n*-BuLi (1.6 M), the last traces in a vacuum of <0.5 mm Hg. After admitting inert gas, cold (0°C) dry diethyl ether (~150 mL) is added to the remaining viscous liquid. The obtained solution is added at ~0°C to the mixture of (3) and diethyl ether. After an additional period of 15 min at 10 - 15°C the product is isolated as described above.

REFERENCES

1. Paley, M.S.; Frazier, D.O.; Abeledeyem, H.; McManus, S.P.; Zutaut, S.E., J. Amer. Chem. Soc., (1992), 114, 3247.
2. Ficini, J.; Barbara, C., Bull. Soc. Chim. France, (1965), 871.
3. Tofimov, B.A., "Vinylpyrroles in the Chemistry of Heterocyclic Compounds", Vol. 48, Part II, p.131, R.A. Jones (ed.), John Wiley, (1992).
4. Prepared by slowly adding at –10 to –15°C a mixture of 0.60 mol of methyl bromide and 150 ml of ether to a mixture of lithium chips (excess) and 200 ml of ether in a way analogous to the preparation of *n*-butyllithium, see Brandsma, L.; Verkruijsse, H.D., Preparative Polar Organometallic Chemistry, Vol. I, p. 18. Springer-Verlag, Heidelberg, (1987).

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