An efficient synthesis of 2-trimethylsilyloxy-4-neopentyl quinoline *via* 3-lithio-1-*tert*-butylallene and phenyl isocyanate

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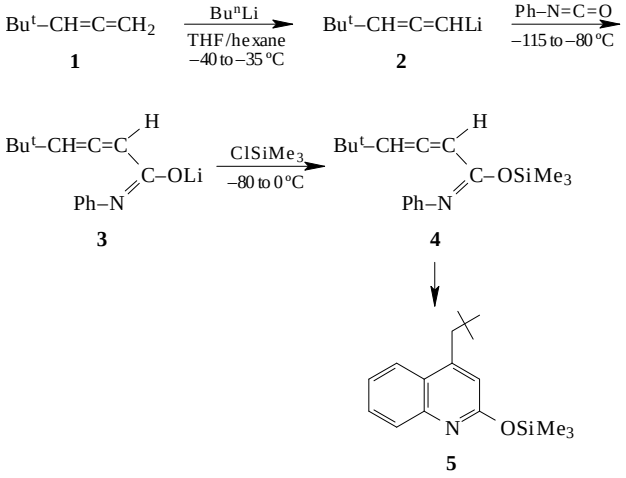
A new method for the preparation of 2-trimethylsilyloxy-4-neopentyl quinoline *via* lithiated *tert*-butylallene and phenyl isocyanate has been developed.

The principal starting compounds in the most important methods for the synthesis of quinolines from non-heterocyclic precursors are benzene derivatives.[1] Direct formation of the quinoline ring *via* isocyanates and organometallic compounds remains unknown. Only a few examples of these reactions leading to amides have been described.[2,3]

As a part of our investigation of the reactions of heterocumulenes with organometallic compounds, leading to important heterocycles, including pyrrole and dihydropyridine derivatives,[4–6] we have developed an efficient synthesis of quinolines, using readily-available starting reagents. In particular, we have shown for the first time that 2,4-disubstituted quinolines can be easily obtained in high yield by the interaction of lithiated allenes and acetylenes with isocyanates and isothiocyanates in a one-pot procedure. Thus, hitherto almost inaccessible 2-trimethylsilyloxy-4-neopentyl quinoline **5** has been synthesised in 75% yield by the addition of lithiated *tert*-butylallene **2** to phenyl isocyanate in a tetrahydrofuran (THF)–hexane solution followed by trimethylsilylation of intermediate **3** and intramolecular cyclization of azatriene **4**.



1 **2** **3** **4** **5**

Intermediate 1,3,4-azatriene **4** was isolated in 95% yield. The structure of the compounds **4** and **5** has been confirmed by IR, ^{1}H and ^{13}C NMR spectroscopy and elemental analysis data.†

More complete results of this study will be given in the next paper.

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† The reaction was performed under anhydrous conditions and in a nitrogen atmosphere. In a typical experiment, *tert*-butylallene (0.11 mol) was introduced into a stirred solution of Bu^{n}Li (0.11 mol) in 70 ml THF and 70 ml hexane cooled to –40 °C. After efficient stirring at –35 °C during 30 min, the reaction mixture was cooled to –115 °C and a solution of phenyl isocyanate (0.11 mol) in 20 ml THF was added in small portions at –100 to –95 °C for 5 min. The reaction mixture was then treated with freshly-distilled trimethylchlorosilane (0.13 mol) at –80 °C. The cooling bath was removed and when the temperature reached 0 °C, dry work-up of the reaction mixture was carried out: removal of solvents on a rotary evaporator, dilution of the rest (a mixture of azatriene **4** with LiCl) with small portions of pentane, filtration of LiCl, removal of pentane on a rotary evaporator. 30 g (95%) of crude **4** (light yellow liquid) was isolated. ^{1}H NMR (90 MHz, CCl_4, standard TMS), δ 5.52 (d, 1H, CH=), 5.32 (d, 1H, CH=), 7.25–6.65 (m, 5H, NPh), 1.05 (s, 9H, Bu^t), 0.30 (s, 9H, OSiMe$_3$).

After refluxing of azatriene **4** during 7–10 min in the presence of *ca.* 1 ml toluene and subsequent distillation *in vacuo* 23.7 g (75%) of quinoline **5** was obtained, bp 135–140 °C (~0.5 mmHg), n_D^{20} 1.5315. IR, ν/cm^{-1}(film): 500, 530, 640, 690, 740, 760, 790, 850–860, 910, 940, 960, 1000, 1030, 1040, 1050, 1070, 1135, 1160, 1190, 1240, 1250, 1260, 1310, 1330, 1350, 1380, 1410, 1440, 1460, 1490, 1510, 1560, 1600, 1630, 1660, 2860, 2900, 2950, 3030, 3050. ^{1}H NMR (300 MHz, $CDCl_3$, standard TMS), δ 6.97 (s, 1H, H-3), 7.86 (d, 1H, H-5), 7.38 (dt, 1H, H-6), 7.60 (dt, 1H, H-7), 8.01 (d, 1H, H-8), 2.96 (s, 2H, CH_2), 1.04 (s, 2H, CH_2), 1.04 (s, 9H, Bu^t), 0.52 (s, 9H, OSiMe$_3$). ^{13}C NMR (75 MHz, $CDCl_3$), δ 160.32 (C-2), 116.28 (C-3), 144.86 (C-4), 124.82 (C-4a), 148.67 (C-8a), 128.66, 128.06, 127.72, 123.19 (C-5–8), 44.28 (CH_2), 32.73 [*C*(Me)$_3$], 30.15 [C(*Me*)$_3$], 0.68 (SiMe$_3$). Found: C 70.78, H 8.75, N 5.26, Si 10.08%; calc. for $C_{17}H_{25}NOSi$: C 71.08, H 8.71, N 4.88, Si 9.76%.