

A NOVEL INDENE SYNTHESIS FROM *N*-PHENYL-1,1-DIPHENYL-2-ETHYLBUT-3-YNYLAMINE

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Summary: When *N*-phenyl-1,1-diphenyl-2-ethylbut-3-ynylamine (1) is treated with 98% formic acid, 2-ethyl-1-methylene-3-phenyl-1H-indene (4, 56%) is produced whereas in 50% formic acid 2-ethyl-1,1-diphenylbut-3-yn-1-ol (98%, 5) is obtained.

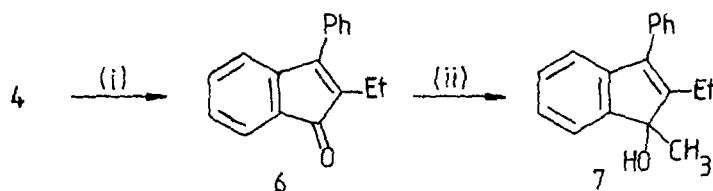
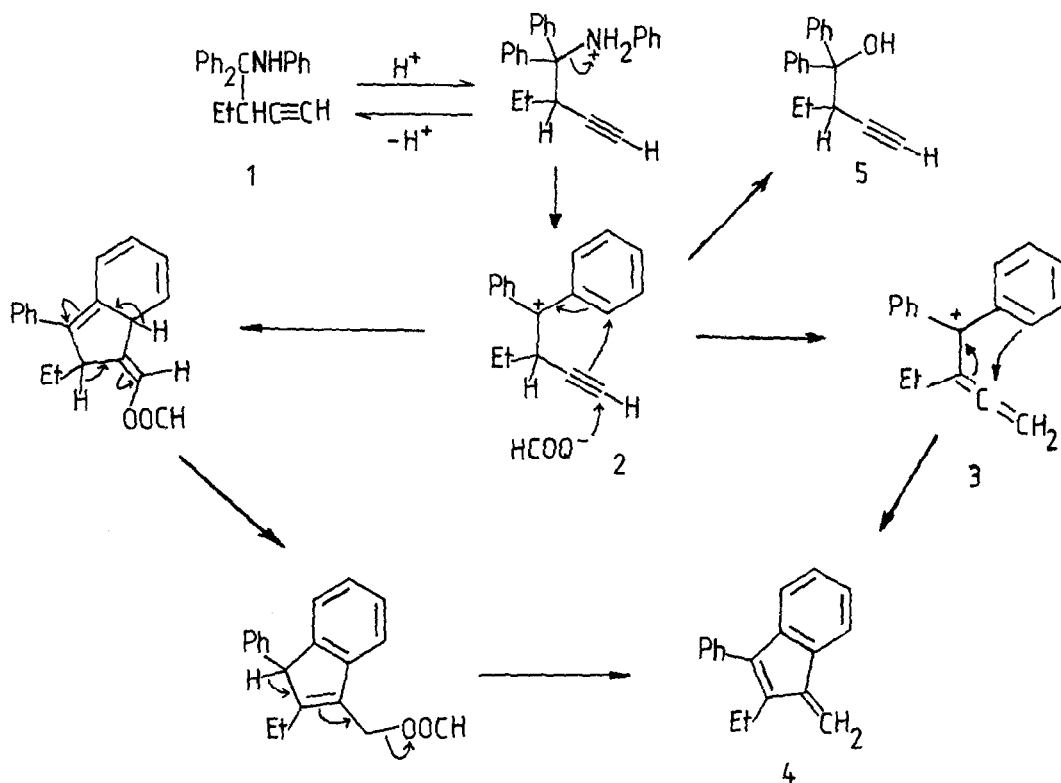
Recently Speckamp and co-workers reported heterocyclic syntheses by α -acyliminium ion-acetylene cyclisations in formic acid.¹ Our novel preparation of alkynylamines from 1,3-dilithio-acetylides and a Schiff's base enabled us to investigate the utility of *N*-phenyl-2-ethylbut-3-ynylamine (1)² in heterocyclic synthesis. We now report that solvolysis in formic acid leads to formation of a methylene-indene (4) or hydrolysis to the alcohol (5).

Reaction of *N*-phenyl-1,1-diphenyl-2-ethylbut-3-ynylamine (1) in 98% formic acid at room temperature (18h) followed by hydrolysis gave 2-ethyl-1-methylene-3-phenyl-1H-indene (4, 56%) as a yellow oil which slowly polymerises but is purified by careful chromatography on silica and elution with light petroleum (b.p. 40-60°).

The structure of the indene (4) was assigned from molecular ion at $M^{+}232$ and the proton n.m.r. spectrum which shows signals at δ 7.55-7.10 (9H, complex, aromatics), 6.05 and 5.74 (each 1H, s, =CH₂), 2.55 (2H, q, CH₂CH₃) and 1.15 (3H, t, CH₂CH₃): the chemical shifts of the exocyclic olefinic protons are in agreement with those found in 1-methylene-1H-indene.³

To account for the formation of the indene (4) it is postulated that protonation of the butynylamine (1) and subsequent elimination of aniline leads to resonance stabilised carbenium ion (2) which cyclises either by involvement of formate ion or by prior allene (3) formation. When *N*-phenyl-1,1-diphenyl-2-ethylbut-3-ynylamine (1) is treated with 50% aqueous formic acid the cation (2) is trapped by solvent and only 2-ethyl-1,1-diphenyl-2-ethylbut-3-yn-1-ol (5, 98%) is obtained (Scheme 1).

Chemical evidence to support the indene structure (4) was obtained from two further reactions. Oxidation of the exocyclic double bond in the indene (4) gave 2-ethyl-3-phenyl-inden-1-one (6, 29%) as a yellow solid, m.p. 87-88°C (Lit.⁵ 89-91°). Reaction of the indenone (6) with an excess of methyllithium in ether at room temperature produced 2-ethyl-1-methyl-3-phenyl-1H-inden-1-ol (7, 31%) as a white solid m.p. 115-116°. The new asymmetric centre at C-1 gives rise to pro-chiral protons in the methylene group of the ethyl side chain seen as characteristic signals at δ 2.52 and δ 2.40 in the proton n.m.r. spectrum at 300 MHz showing geminal and vicinal coupling (J 7.5 and 14.6 Hz).



Reagents: (i) KMnO_4 , C_6H_6 , 18-crown-6, room temperature, 18h (29%).

(ii) MeLi , Et_2O , 18h; 22% NH_4Cl , HCl (31%).

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