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1,7-Electrocyclisation of Non-Stabilised Azomethine Ylides

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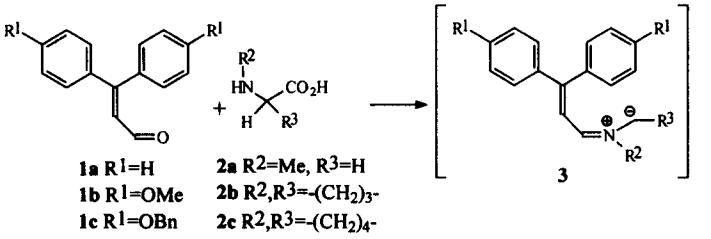
Abstract: Non-stablilised α,β;γ,δ-unsaturated azomethine ylides **3** were generated by the decarboxylation method from 3,3-diarylpropenals **1** and secondary amino acids **2**. 1,7-Electrocyclisation of these azomethine ylides, followed by a 1,5-hydrogen shift, gives 2,3-dihydro-1*H*-2-benzazepines **4**.

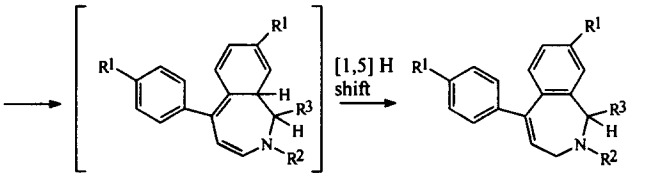
In this communication we describe the novel 1,7-electrocyclisation of non-stabilised azomethine ylides **3**, generated from 3,3-diarylpropenals **1** and *N*-substituted α-amino acids **2** using the decarboxylation method (Scheme 1).[1]



1a R^1=H **1b** R^1=OMe **1c** R^1=OBn

2a R^2=Me, R^3=H **2b** R^2,R^3=-$(CH_2)_3$- **2c** R^2,R^3=-$(CH_2)_4$-

3



4a R^1=H, R^2=Me, R^3=H
4b R^1=OMe, R^2=Me, R^3=H
4c R^1=OBn, R^2=Me, R^3=H
4d R^1=H, R^2,R^3=-$(CH_2)_3$-
4e R^1=OBn, R^2,R^3=-$(CH_2)_3$-
4f R^1=H, R^2,R^3=-$(CH_2)_4$-

Scheme 1

The intermediacy of the azomethine ylides **3** was shown by the trapping of ylide **3a** with *N*-phenylmaleimide to give the two isomeric cycloadducts **5a** and **5b** (*endo* - *exo* ratio 1:1) (Scheme 2). The structure and stereochemistry of the *exo*-cycloadduct **5a** was established by 2D-COSY and ^{1}H nOe experiments. The irradiation of H-2α gave a large enhancement of H-2a and one of the H-6 methylene protons, while the irradiation of H-2 gave an enhancement of only the *N*-Me singlet.

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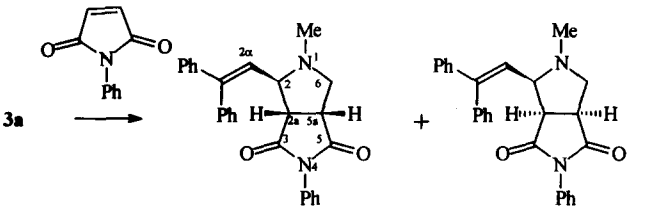

5a **5b**

Scheme 2

The reaction of β-phenylcinnamaldehyde **1a** with sarcosine **2a** (2 equiv.), in refluxing *p*-xylene, gave 2,3-dihydro-2-methyl-5-phenyl-1*H*-2-benzazepine **4a** in almost quantitative yield, *via* a 1,7-electrocyclisation followed by a 1,5-hydrogen shift. The ^{1}H n.m.r. spectrum of **4a** shows the C-3/C-4 protons as a characteristic AX_2 system with the two H-3 protons as a doublet (δ 2.90, J_{AX} = 7.3 Hz) and H-4 as a triplet (δ 6.47, J_{AX} = 7.3 Hz).[2] In addition, the C-1 methylene protons and the *N*-methyl give singlets at δ3.61 and 2.47 respectively. Our first attempts at purification of the crude products proved difficult as chromatography on silica gel resulted in decomposition. Separation from the minor, more coloured, impurities was, however, effected on neutral alumina. The reaction of the 4-substituted derivatives **1b,c** with sarcosine **2a** also gave azomethine ylides which underwent 1,7-electrocyclisation to the corresponding 2-benzazepines **4b,c** in excellent yields (94 and 95% respectively). The use of cyclic secondary amino acids, namely proline **2b** and pipecolinic acid **2c**, gave rise to the formation of the more complex pyrrolo[1,2-*a*][2]benzazepine[3] **4d** (42%), **4e** (38%) and pyrido[1,2-*a*][2]benzazepine **4f** (33%) ring systems, in a single step. The moderate yields for the formation of these more complex ring systems are due to decomposition on chromatographic separation, even on neutral alumina.

References

1. Nyerges, M.; Balazs, L.; Kádas, I.; Bitter, I.; Kövesdi, I.; Tôke, L. *Tetrahedron* 1995, **51**, 6783.
2. All compounds gave satisfactory analytical and spectroscopic data. For example; **4a** (85%), pale yellow oil (Found: MH$^+$, 236.144. Calc. for $C_{17}H_{18}N$: *MH*, 236.144); δ_H ($CDCl_3$) 2.47 (3H, s,NMe), 2.90 (2H, d, *J* 7.3 Hz, H-3), 3.61 (2H, s, H-1), 6.47 (1H, t, *J* 7.3 Hz, H-4), 7.10 (1H, m, H-9), 7.25-7.35 (7H, m); 7.39 (1H, m, H-6); δ_C ($CDCl_3$): 43.0 (NMe), 51.8 (CH_2), 58.0 (CH_2), 124.0 (CH), 127.4 (CH), 127.6 (CH), 127.8 (CH), 128.2 (2xCH), 128.4 (2xCH), 129.1 (CH), 129.8 (CH), 136.8 (quat.), 140.3 (quat.), 140.9 (quat.), 147.0 (quat.); ν_{max} (Nujol/cm^{-1}) 1600 (C=C); CIMS *m/z* 236 (MH$^+$, 81 %); 235 (M$^+$, 100%), 234 (87), 193 (30), and 144 (31).
3. Meyers, A. I.; Hutchings, R. H.. *Tetrahedron*, 1993, **49**, 1807.