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Synthesis of Novel Protected Hemiaminal N-Methoxymethyl-N'-Methyl-9,9'-Biacridylidene from Lucigenin

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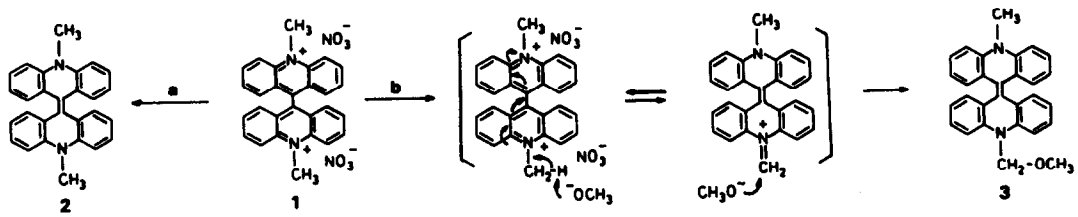
Abstract: A novel protected hemiaminal, N-methoxymethyl-N'-methyl-9,9'-biacridylidene **3** has been identified as the major product on nucleophilic addition of concentrated methanolic alkali to lucigenin, **1**, while reductants such as hydrazine derivatives lead to N,N'-dimethyl-9,9'-biacridylidene **2**

As part of a project to develop novel chemiluminescent lucigenin homologues via addition of nucleophiles to N,N'-dialkyl-9,9'-biacridinium nitrates we have been examining the nucleophilic addition of hydrazines and alcohols to lucigenin **1**.

The nucleophilic addition of hydrazine hydrate and asymmetric N,N-dimethyl hydrazine to lucigenin in methanol produces as major product N,N'-dimethyl-9,9'-biacridylidene (DBA) **2**. The best chemical yield was obtained with N,N-dimethyl-hydrazine (74 %). The spectroscopic data of the major reaction product were identical with those of DBA given in the literature[1].



a: NH_2-NH_2.H_2O; $(CH_3)_2N$-NH_2 / CH_3OH, reflux.
b: NaOH / CH_3OH, reflux.

Scheme

We discovered that concentrated methanolic alkali reacts with lucigenin not in the expected way (nucleophilic addition of methanol to C9-C9' position of lucigenin, double pseudo- Michael addition) but gives rise to the protected hemiaminal **3** in pure form and in very good yield (scheme). The identification of **3** was

confirmed by two-dimensional ^{1}H- and ^{13}C NMR analysis and compared with the spectroscopic data of DBA and lucigenin. Based on the differences in chemical shifts as well as the integral of the two N-methyl groups, the structure of the hemiaminal **3** was assigned.

In addition, the high resolution mass spectrum of compound **3** (M+ = 416,1899) shows two characteristic peaks at m/e= 371 (base peak, M$^+$-45) and 45 (10) which is compatible with the hemiaminal structure **3**

The reaction mechanism would involve deprotonation of a N-methyl group followed by attack of the methoxide anion[2] at the methylide (iminium salt) carbon atom (scheme). Similar results, i.e. nucleophilic addition to iminium salts have been observed on treatment of iminium salts with organometallic compounds[3-5] enol borinates[6], diazomethane[7] and cyanide[8] anion to yield exclusively tertiary amines. Iminium salts, normally give tertiary amines directly just by addition of carbanions[7]. To our knowledge this is the first nucleophilic addition of alcohol to a conjugated iminium salt or methylide such as the lucigenin ones and there is no apparent reason for bi-pyridinium or bi-quinolinium salts not to react the same way.

Encouraged by results with the n-butoxy-analog, we are currently investigating the use of lucigenin as d1/a1-umpoled synthon with a variety long N-alkyl chain alcohols as nucleophiles to produce novel N-alkoxymethyl-N'-methyl-biacridinium salts as chemiluminescent "monomers" for organized molecular assemblies.

Procedure for the synthesis of 3

Lucigenin[9] (233 mg, 0.45 mmol) was dissolved in 50 ml methanol in a 250 ml conical flask. To the warmed solution 50 ml methanol containing 1.0 g sodium hydroxide were added. After 2 hours at reflux the undissolved product was filtered off, washed with cold methanol and dried under reduced pressure. Chemical yield: 120 mg (64 %). m.p. 275°C $C_{29}H_{24}N_2O$ (416.5) Calc. C 83.62 H 5.80 N 6.74 found: C 83.38 H 5.87 N 6.47

IR(KBr): ν 1585, 1450, 1265, 1060, 1030, 740 cm^{-1}. M.S.: m/e 417 (3, M$^+$+1), 416 (15, M$^+$), 386 (6), 372 (27), 371 (100, M$^+$ -CH_2OCH_3), 45 (10, CH_2OCH_3). ^{1}H NMR ($CDCl_3$/TMS, 250 MHz) : δ 3.56 (s, 3H, NCH_3); 3.61 (s, 3H, OCH_3); 5.42 (s, 2H, NCH_2O); 6.82 (mc, 4H$_{arom}$); 7.08 (mc, 6H$_{arom}$); 7.27 (mc, 8H$_{arom}$). ^{13}C NMR ($CDCl_3$/TMS, 62.9 MHz): δ 33.3 (NCH_3); 54.7 (OCH_3); 79.6 (NCH_2O); 112.4; 114.5; 119.9; 120.8; 124.5 (C=C); 127.1; 127.2; 128.1; 128.2; 143.6; 145.0

References and Notes

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9. Lucigenin was purchased from Aldrich, Milwauke, USA and used without further purification.

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