Aminodioxetans. Preparation of the Stable 3,3-Dimethyl-4-[*N*-(2-methyl-1-hydroxypropyl)anthrylamino]-1,2-dioxetan

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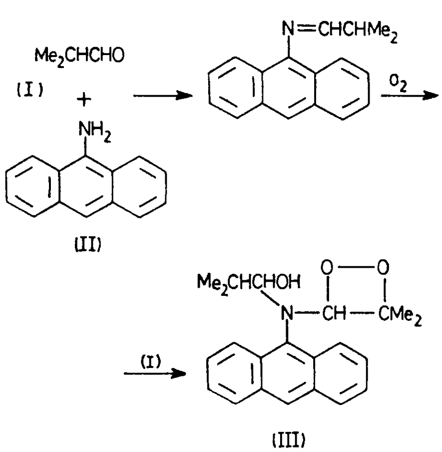
Summary A simple method is reported for the preparation of a stable amino-1,2-dioxetan from 9-anthrylamine and isobutyraldehyde in the presence of atmospheric oxygen.

McCapra *et al.*[1] have demonstrated that the Schiff base from 4-aminopyridine and isobutyraldehyde (I) emitted light in the Me_2SO–$KOBu^t$–O_2 system. They considered that this chemiluminescence was a bioluminescence model for *Latia neritoides*, and postulated the intermediacy of an amino-1,2-dioxetan. Although some stable dioxetans have recently been prepared,[2] a stable aminodioxetan has not been reported except for 3-morpholino-3,4-butano-1,2-dioxetan which could be isolated at −78 °C.[3] We now report a simple preparation of a stable aminodioxetan from 9-anthrylamine (II) and (I).



Scheme

Pale yellow prisms of (III), m.p. 113—113·5 °C (decomp.), were obtained in 54% yield from a solution of (I) and (II) (molar ratio 3 : 1) in n-hexane which had been kept in the dark at 30 °C for a few days in the presence of atmospheric oxygen. The structure of (III) was established from elemental analysis ($C_{22}H_{25}NO_3$), chemical reactions (see below), and spectral data; *m/e* 351 (M^+), ν_{max} 3380 cm^{-1} (OH), δ ($CDCl_3$) 0·72 (d, 6H, *J* 6 Hz, Me_2CH), 1·51 and 1·71 (2 × s, each 3H, Me_2C–OO),[4] 1·55–1·92 (m, 1H, Me_2CH), 4·28 (br.s, 1H, exchangeable, OH), 4·80 (s, 1H, N–CH–OO), 4·82 (d, 1H, *J* 4 Hz, C*H*OH), and 7·44—8·60 (m, 9H, ArH). The absence of OOH[5] and –N=CH– units in (III) was confirmed on the basis of its n.m.r. and i.r. spectra. A solution of (III) in toluene emitted light on heating to 100 °C. Pyrolysis of (III) in a sealed tube gave *N*-formylanthrylamine (IV), (I), and Me_2CO in good yields. The aminodioxetan (III) showed chemiluminescence in the Me_2SO–$KOBu^t$–Ar system. The chemiluminescence spectrum of (III) (λ_{max} 542 nm) was in accord with the fluorescence spectrum of (IV) in the same system.

A mechanism for the formation of (III) is shown in the Scheme. The stability of (III) may be due to steric protection of the substituents on the aminodioxetan ring.

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