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Amidoethylation of Anthracene Hydride by *N*-Aroylaziridines: Inner-sphere Single Electron Transfer (SET) and Radical Coupling confirmed†

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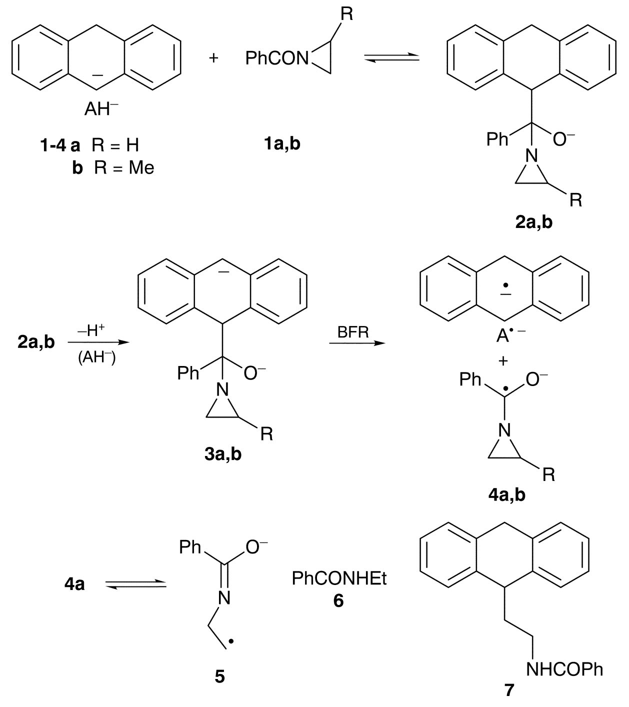
Regioselectivity (near 1:1) of substitutive ring opening of 1-benzoyl-2-methylaziridine by anthracene hydride is incompatible with common nucleophilic attack and thus confirms the radical coupling path.

Reactions of *N*-aroylaziridines with excess anthracene hydride (AH^-) may be exemplified by means of **1a** (Scheme 1). Aziridino ketyl **4a** is an essential intermediate[3] generated by benzylic fragmentation (BFR)[4] of the rapidly formed[3] carbonyl adduct **2a**. Homolytic ring cleavage of **4a** affords the amidatoalkyl radical **5a**, a precursor of the main product **6**. The second product is **7**.

When the aziridine ring of **1a** carries substituents, analogues of **7** are obtained[3] unless they arise from 2-phenylaziridines and are unstable under usual conditions.[3,5] The assumption[3] that **7** and its analogues are formed by coupling of amidatoalkyl radicals with anthracenide $A^{\bullet -}$ was supported by a regioselectivity of ring opening that seemed to exclude a direct S_N2-like path to analogues of **7** and hence also to **7**. Subsequently it was found[6] from a study of 1-acyl-2,2-dimethylaziridines that S_N2-like ring opening may require planarization of the nitrogen pyramid thereby shifting the mechanism to a borderline type whose regioselectivity is compatible with the AH^- results. This reopened the mechanistic question since the very fast initial carbonyl attack is reversible.[7]

Ring opening of 1-acyl-2-methylaziridines by strong nucleophiles was recently[8] shown to strongly prefer cleavage of the N–CH_2 bond. AH^- and 2-methyl-1-pivaloylaziridine provided a mixture of products (total 94%) with an overall regioselectivity isopropylamides:*n*-propylamides of 35:1. The reaction of xanthenyl anion (oxa analogue of AH^- devoid of the BFR path) with **1b** yielded 82% of benzoylxanthene and 14.5% of amidoethylated xanthenes with an iso to normal regioselectivity of 28:1. Thus, one may expect a ratio of about 30:1 if **i-10** and **n-10** (Scheme 2) are formed from **1b** and AH^- only, or mainly, by nucleophilic ring opening.

Two three-day runs of 10 mmol of **1a** with 16 mmol of AH^-Li^+ in 200 ml of THF provided 58% (47%) of isopropylamide **i-9**, 14% (18%) of *n*-propylamide **n-9**, 9% (4%) of **i-10** and 9% (5%) of **n-10** (values in parentheses are the yields of the second run). The yields of both **10** are crude yields in the sense that they were estimated by ^1H NMR from fractions containing minor amounts of unknown products, probably isomers of **10**, one of them being **11** (see below). But the yield ratios $i:n = 1$ (0.8), determined from the methyl doublets at 1.21 and 0.94 ppm, are sufficiently reliable. These ratios of isomeric **10** are far from the 30:1 ratio expected for an S_N2 mechanism. Both **10** arise consequently only or nearly so from coupling of anthracenide $A^{\bullet -}$ (generated by BFR) with amidatoalkyl radicals **i-8** and **n-8**. Moreover, coupling with position 1 of $A^{\bullet -}$ obviously formed traces of **11** (one or two products with isomeric side chains). **11** was identified in the inseparable mixture of isomeric **10** by characteristic ^1H NMR signals for the non-aromatic double bond. A doublet (*J* 10.4) for H-4 at 6.70 ppm shows fine splitting (*ca.* 1.1 Hz) of the lines from coupling with H-10. A doublet (*J* 10.4) of approximated triplets (*J ca.* 5) at 6.08 ppm comes from H-3, the triplets indicating attachment of the amidatopropyl chain to position 1. Olefinic and additional aromatic signals are in accord with those of 2-vinylnaphthalene.[10]



Scheme 1

There were at least four methyl doublets (*J ca.* 6.8 Hz, at 1.02, 1.11, 1.31 and 1.42 ppm) in addition to those of both **10**. This is compatible with a mixture of **i-11** and **n-11** when one considers diastereoisomerism. However, part of these signals may come from structural isomers of **11**, *e.g.* Y carried in position 2. Weak signals in the range of 5.9–6.7 ppm point to isomerism in the non-aromatic ring.

Cleavage **4b** → **i-8** will be kinetically controlled (*cf.* ref. 9) and reduction of the amidatoalkyl radicals by a second **4b** forms probably the primary carbanion faster than the secondary one. It is therefore not surprising to find much more **i-9** than **n-9**.

Experimental

The reactions were performed as described in ref. 4 starting with 17 mmol of dihydroanthracene AH_2 and 16 mmol BuLi (hexane). The reactions were quenched with acetic acid. The residue obtained after the usual workup was chromatographed (silica gel Merck, 0.063–0.200 mm, 40 cm × 4 cm, toluene–ethyl acetate 9:1); compo-

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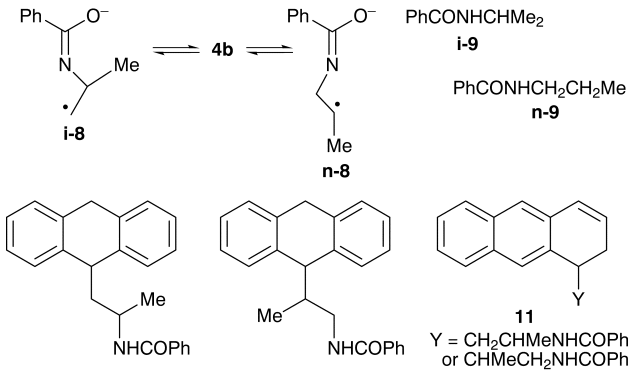

Scheme 2

site fractions were analyzed by ^{1}H NMR ($CDCl_3$, Me_4Si internal). *J* values are given in Hz.

Run 1 provided hydrocarbons and their oxidation products; 72 mg of unknown products and 120 mg of a 3:1 mixture of **i-10** (90 mg) and **n-10** (30 mg) followed. A crystal of **i-10** could be manually picked out. Continued elution yielded 482 mg of a 1:1.2 mixture of **i-10** (219 mg, total 309 mg = 9%) and **n-10** (263 mg, total 293 mg = 9%) containing a trace of **11** (^{1}H NMR data given in the text). Further elution gave 146 mg of **i-9** and 1022 mg of a mixture of 798 mg (total 944 mg = 58%) of **i-9** and 224 mg (14%) of **n-9**.

i-10: mp 192–194 °C; ν_{max}/cm^{-1} 3303 (NH), 1636 (amide I), 1538 (amide II); δ_H 1.21 (d, *J* 6.6, Me), 1.87 (m, $NCCH_2$), 3.88 (d, *J* 18.4, 10-H pseudo eq), 4.08–4.31 (m, 9-H and NCH), 4.12 (d, *J* 18.3, 10-H pseudo ax), 5.90 (d br, *J* 8.2, NH), 7.17–7.32 (m, 8 ArH), 7.38–7.42 (m, *m*-H and *p*-H of Ph), 7.63 (m, *o*-H of Ph).

n-10 (in mixture with **i-10**): δ_H 0.89 (d, *J* 6.8, Me) (m, NCCH), 3.35 (dt_{approx}, *J* 13.8 and *ca.* 6.0, 1 H of NCH_2), 3.49 (dt_{approx}, *J* 13.8 and *ca.* 6.7, 1 H of NCH_2), 3.81 (d, *J* 7.4, 9-H), 3.85 (d, *J* 18.3, 10-H pseudo-eq), 4.13 (d, *J* 18.3, 10-H pseudo-ax), 5.84 (s br, NH), aromatic signals cannot be distinguished from those of **i-10**.

Mixture of **i-10** and **n-10**: (Found: C, 84.3; H, 6.9; N, 4.0. $C_{24}H_{23}NO$ requires C, 84.4; H, 6.8; N, 4.1%); ν_{max}/cm^{-1} 3313 (NH), 1631 (amide I), 1540 (amide II).

Run 2 provided hydrocarbons and their oxidation products; 65 mg of unknown products and 219 mg of a mixture of **i-10** (91 mg) and **n-10** (128 mg) followed. Further elution yielded 182 mg of a mixture containing mainly (more than 90 mg totalling to 279 mg = 9%) **10** in a ratio of 55 mg (total 146 mg = 4%) of **i-10**: 35 mg (total 163 mg = 5%) of **n-10**. This mixture contained also some **11**. Continued elution provided 84 mg of **i-9** and 976 mg of a mixture consisting of 687 mg (total 771 mg = 47%) of **i-9** and 289 mg (18%) of **n-9**.

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