9 Syntheses of $^{13}$C-Labelled Polycyclic Aromatic Compounds

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9.1 Introduction

The use of stable isotopes, especially $^{13}$C, is well established for investigation of metabolic pathways or biosyntheses, as a tool in diagnostic medicine and to generally trace the fate of organic compounds in the environment. Excellent techniques to monitor the isotope in labelled compounds include nuclear magnetic resonance ($^{13}$C-NMR-spectroscopy) (Marshall 1983; Breitmaier and Voelter 1987) and (combustion) isotope-ratio-monitoring mass spectrometry (IRM-MS) (Merrit et al. 1994; Wong et al. 1995; Newman 1996; Brenna 1999).

In general labelled model compounds are required to trace biotic and abiotic mechanisms in the degradation of polycyclic aromatic hydrocarbons (PAH), to screen the involvement of PAH in the formation of bound residues in the soil as well as to investigate the chemical interactions between PAH and the humus matrix.

In this paper we report on the design and completion of efficient and economic syntheses of $^{13}$C-labelled PAH. The following 13 compounds were synthesised (for chemical structures see fig. 9.1): [1-$^{13}$C]-naphthalene (1), [1-$^{13}$C]-naphthol (2), [α-$^{13}$C]-1,2-dimethylnaphthalene (3), [5-$^{13}$C]-acenaphthylene (4), [5-$^{13}$C]-acenaphthene (5), [9-$^{13}$C]-anthracene (6), [1-$^{13}$C]-phenanthrene (7), [1-$^{13}$C]-phenanthren-1-ol (8), [4-$^{13}$C]-phenanthrene (9), [9-$^{13}$C]-phenanthrene (10), [3-$^{13}$C]-fluoranthene (11), [3a-$^{13}$C]-pyrene (12) and [7-$^{13}$C]-benzo[a]pyrene (13).

9.2 Results and Discussion

In our syntheses we attempted to follow a generally applicable route which involves anellation of a suitable carboxylic acid (or its acid chloride) by intramolecular Friedel-Crafts acylation followed by aromatisation. The $^{13}$C-label was introduced into the corresponding carboxylic acid during a late step via reaction of a Grignard compound (prepared from the corresponding
bromoalkylaromates) and ¹³C-carbon dioxide (prepared from commercially available sodium ¹³C-carbonate). In this step we preferred ¹³C-carbon dioxide rather than ¹³C-cyanide as an alternative C 1-unit, as it is cheaper, easy to handle, and immediately yields the desired acid upon work up. The Friedel-Crafts acylation was carried out either with acid using polyphosphoric acid or with the acid chloride using tin tetrachloride. After removal of the carbonyl group