Synthesis of Some Substituted Adamantanetriones

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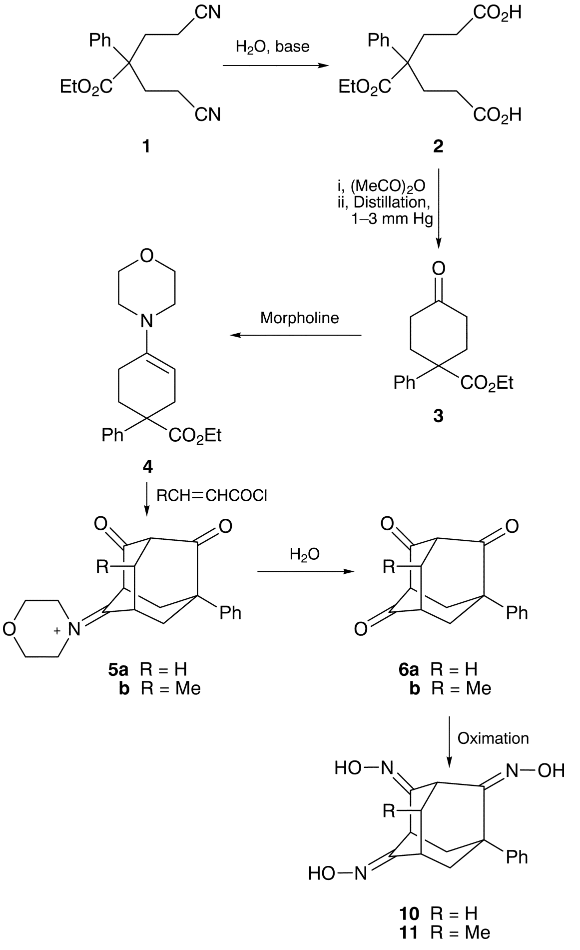
Following the same general procedure employed for the synthesis of substituted adamantane-2,4-diones which we reported previously[6,7] we now herein report the synthesis of substituted adamantane-2,4,6-triones **6a** and **6b**.

The morpholine enamine **4** of ethyl 1-phenyl-4-oxocyclohexane-1-carboxylate **3** prepared following the reported procedure,[9] reacted with acryloyl and crotonoyl chlorides giving 1-phenyladamantane-2,4,6-trione **6a** and 10-methyl-1-phenyladamantane-2,4,6-trione **6b**† respectively in good yields. The structures of the adamantane derivatives were established from their spectral properties. Preparation and characterization of oximes **10** and **11** of compounds **6a** and **6b** afforded additional evidence for their structures (Scheme 1).

The crystalline compounds **6a** and **6b** gave informative ^{1}H NMR spectral data in CDCl$_3$. It was possible to assign all the protons by running two-dimensional (^{1}H—^{1}H COSY) NMR spectra and the coupling constants were determined from the one-dimensional spectra. In both the compounds **6a** and **6b** the bridgehead protons at positions **3** and **5** appeared downfield due to the adjacent carbonyl groups. The protons at these positions in **6b** were shifted slightly upfield in comparison to **6a** due to the anisotropic effect of the CH$_3$ group in the 10 position. The methylene protons of positions 8 and 9 individually appeared as singlets in each of **6a** and **6b**. In each of these compounds the protons at position 8 were more deshielded than those at position 9 due to the phenyl group at position 1 (δ 0.16 in the case of **6a** and δ 0.13 in the case of **6b**). The stereochemistry at position 10 in **6b** is evident from the relatively high δ value of the protons at this position which is indicative of its equatorial conformation.[6,7] This in turn indicates the axial conformation of the 10-CH$_3$ group in **6b**.



Scheme 1

Similar observations were made for the shielding and deshielding effects on carbon at different positions of compounds **6a** and **6b**. The chemical shifts and substituent pattern of carbons in **6b** were assigned with the help of ^{1}H—^{13}C COSY and DEPT NMR spectroscopy. By analogy with **6b** the positions of the carbon atoms in **6a** were ascertained. The shielding and deshielding of different carbons were explained on the basis of the substitution chemical shift effect and the *γ-anti* effect.[8] This further confirmed the stereochemistry at position 10 for compound **6b**. In their mass spectra compounds **6a** and **6b** showed molecular ions at *m*/*z* 254 and 268 respectively.

Techniques used: IR, ^{1}H and ^{13}C NMR, and mass spectrometry

References: 10

Schemes: 2

Table 1: Proton NMR spectral data for compounds **6a** and **6b**

Table 2: Carbon-13 NMR spectral data for compounds **6a** and **6b**

Table 3: Carbon-13 NMR spectral data for compound **3**

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†In defining axial and equatorial positions in these polycyclic compounds the Snatzke[10] convention was followed.