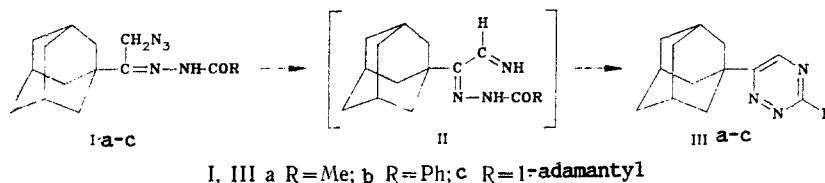


THERMOLYSIS OF α -AZIDO KETONE ACYLHYDRAZONES - A NEW
ROUTE TO 1,2,4-TRIAZINES

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We have established that the thermolysis of α -azidomethyl 1-adamantyl ketone acylhydrazones I leads to 3-substituted 6-(1-adamantyl)-1,2,4-triazines III. The reaction probably proceeds through a step involving the formation of imine II, the intramolecular condensation of which leads to the aromatic 1,2,4-triazine system.



The aromatic character of the compounds obtained is confirmed by their UV spectra and PMR spectra, in which there are signals at 8.8-9.0 ppm, which belong to the 5-H protons of the triazine ring.

6-(1-Adamantyl)-3-methyl-1,2,4-triazine (IIIa), $\text{C}_{14}\text{H}_{19}\text{N}_3$. This compound, with mp 102-103°C (from aqueous MeOH), was obtained in 58% yield by refluxing acetylhydrazone Ia in xylene. UV spectrum (MeOH): λ_{max} 237 nm ($\log \epsilon$ 3.72). PMR spectrum (d_6 -DMSO): 1.77-2.35 (15H, m, Ad), 2.74 (3H, s, CH_3), 8.86 ppm (1H, s, 5-H). The following compounds were similarly obtained.

6-(1-Adamantyl)-3-furyl-1,2,4-triazine (IIIb), $\text{C}_{19}\text{H}_{21}\text{N}_3$. This compound was obtained in 68% yield and had mp 115-117°C (from aqueous 2-propanol). UV spectrum (MeOH): λ_{max} 261 nm ($\log \epsilon$ 4.22). PMR spectrum (d_6 -DMSO): 1.8-2.1 (15H, m, Ad), 7.6-8.5 (5H, m, Ph), 9.03 ppm (1H, s, 5-H).

3,6-Di(1-adamantyl)-1,2,4-triazine (IIIc), $\text{C}_{23}\text{H}_{31}\text{N}_3$. This compound was obtained in 73% yield and had mp 240-242°C (from aqueous 2-propanol). UV spectrum (MeOH): λ_{max} 241 nm ($\log \epsilon$ 3.73). PMR spectrum (d_6 -acetone): 1.81-2.08 (30H, m, Ad), 8.75 ppm (1H, s, 5-H).

The results of elementary analysis were in agreement with the calculated values.

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