Light induced 2+2 cycloaddition reaction of adenine in acidic and alkaline medium and determination of molecular structures

Amitbodh Upadhyay, Deepali Pradhan & Shubha Jain

School of Studies in Chemistry, Vikram University, Ujjain 456 010, India

Received 29 May 1998; accepted (revised) 25 November 1998

The effect of pH on photolysis of adenine has been studied. Adenine \( \text{1} \) when subjected to irradiation by UV light, undergoes 2+2 cycloaddition, giving rise to products \( \text{2} \) and \( \text{3} \) respectively. In acidic medium, dimerization is preceded by deamination.

Light induced reactions of purines with alcohols and amines have been studied widely\(^1\)\(^6\). Herein we report the effect of pH on the photolysis of adenine in acidic and alkaline medium.

Results and Discussion

When an aqueous and acidic solution of adenine is irradiated by UV light, it undergoes deamination followed by 2+2 cycloaddition (dimerization) (Scheme 1), whereas an aq. and alkaline solution of adenine undergoes direct 2+2 cycloaddition on UV irradiation (Scheme II). The reason for this difference may be that in acidic medium, the -NH\(_2\) group of adenine gets protonated and thus deamination is facilitated, whereas in alkaline medium, this facility is not there. The structures of 2 and 3 have been supported by spectral data and elemental analysis.

Experimental Section

An alcoholic solution of adenine (2 g) was irradiated by medium pressure mercury arc lamp after making it acidic (pH 5) and alkaline (pH 9), separately. Benzophenone was used as sensitizer. The...
Figure 1—Fragmentation pattern for compound 2 (w=weak; b=base peak)

Figure 2—Fragmentation pattern for compound 3
progress of the reaction was monitored by TLC in butanol : acetic acid : water (12:3:5 v/v) solvent system. In acidic medium, the reaction was completed in 35 hr. and in alkaline medium, it completed in 40 hr. The products (2 and 3) were recrystallized from ethanol. 2 : m.p. 352-54°C, yield ~0.8 g; Anal. Found: C, 44.48; H, 3.06, N, 41.2; Calc. for C\textsubscript{10}H\textsubscript{12}N\textsubscript{3}O\textsubscript{2}: C, 44.11; H, 2.9; N, 41.18%. IR: 3300 (br, N-H and O-H stretching), 1695 (C=N and C=O stretching), 1610 (C=C stretching) cm\textsuperscript{-1}; \textsuperscript{1}H NMR: \delta 6.6 (br, 4-NH and -OH protons), 8.55 (2-CH protons four membered ring), 9.15 (2-CH protons, 6 membered ring); Mass: m/z 270 (weak, M\textsuperscript{+} peak), 135 (base peak), 136 (M+1 peak due to nitrogen) (Fragmentation data in Figure 1). 3 : m.p. 330-32°C, yield ~0.9 g. Anal. Found: C, 44.36; H, 3.77; N, 51.9. Calc. for C\textsubscript{10}H\textsubscript{12}N\textsubscript{3}O\textsubscript{2}: C, 44.44; H, 3.7; N, 51.85%. IR 3310 (s, N-H stretching), 1610 (C=N stretching), 1600 (C=C stretching) cm\textsuperscript{-1}; \textsuperscript{1}H NMR: \delta 2.15 (2-CH protons alicyclic), 3.45 (4-NH\textsubscript{2} protons), 8.15 (2-CH protons, 6 membered ring); Mass: m/z 270 (weak, M\textsuperscript{+} peak), 135 (base peak), 136 (M+1 peak due to nitrogen) (Fragmentation data in Figure 2).

References