

Photo-dealkylation of C-8-Hydroxyalkylpurines

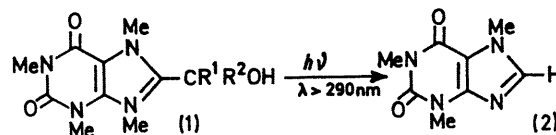
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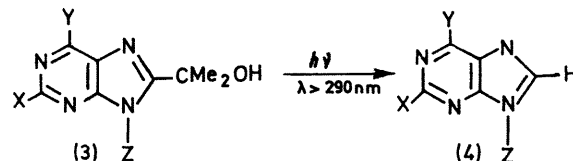
Summary C-8-Hydroxyalkylpurines and purine nucleosides upon irradiation are transformed into the original purines.

PHOTOCHEMICAL reactions of purines and purine nucleosides with alcohols have been shown to lead to the substitution of an α -hydroxyalkyl group for a hydrogen atom in the purine nucleus.¹⁻³ The location of the new substituent depends on the purine involved, and with purines from nucleic acids alkylation takes place at the C-8 position.³ These reactions were further applied to the production of DNA with purines modified at C-8.⁴ We report the photo-dealkylation of C-8-hydroxyalkylpurines and purine nucleosides which leads to the regeneration of the original purine or purine nucleoside. The reactions were initiated with light $\lambda > 290$ nm in the presence of photosensitizers. In some cases, mainly with the nucleosides, reaction could be induced in the absence of a photosensitizer but with lower yields. The reactions studied are summarized (Table).

In a typical experiment, a solution of a C-8-hydroxyalkylcaffeine (100 mg) and *NN*-dimethylaniline (100 mg) in methanol (75 ml) was irradiated† for 24 h. The excess



- (a) $R^1 = R^2 = H$;
 (b) $R^1 = H, R^2 = Me$;
 (c) $R^1 = R^2 = Me$



- (a) $X = H, Y = NH_2, Z = H$;
 (b) $X = H, Y = NH_2, Z = \text{ribose}$;
 (c) $X = NH_2, Y = OH, Z = \text{ribose}$.

of reagents was removed under reduced pressure and the

† Irradiation was carried out with a Hanovia 450W high-pressure mercury-vapour lamp with a Pyrex filter.

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C-8-substituted purine	Sensitizer	Product	Yield ^a (%)
Caffeine-8-CH ₂ OH (1a) ..	—	Caffeine (2)	trace
	Carbazole	" "	12
	<i>NN</i> -Dimethylaniline ..	" "	30
Caffeine-8-CHMeOH (1b) ..	—	" "	trace
	Carbazole	" "	12
	<i>NN</i> -Dimethylaniline ..	" "	31
Caffeine-8-CMe ₂ OH (1c) ..	—	" "	7
	Carbazole	" "	56
	<i>NN</i> -Dimethylaniline ..	" "	74
	Iron(II) ammonium sulphate	" "	22
	Histidine	" "	26
Adenine-8-CMe ₂ OH (3a) ..	—	Adenine (4a)	trace
	<i>NN</i> -Dimethylaniline ..	" "	43
Adenosine-8-CMe ₂ OH (3b)	—	Adenosine (4b)	21
	Carbazole	" "	37
	<i>NN</i> -Dimethylaniline ..	" "	73
Guanosine-8-CMe ₂ OH (3c)	—	Guanosine (4b)	31
	<i>NN</i> -Dimethylaniline ..	" "	60

^a Yields are based on purine used.

residue was chromatographed on silica gel to isolate caffeine. preparative paper chromatography on Whatman No. 17
The other purines and purine nucleosides were isolated by paper with H₂O-NH₄OH-BuⁿOH as eluant.³

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⁴ H. Steinmaus, D. Elad, and R. Ben-Ishai, *Biochem. Biophys. Res. Comm.*, 1970, **40**, 1021.