

Photocycloaddition of Methanol to Dihydropyridinium Salts

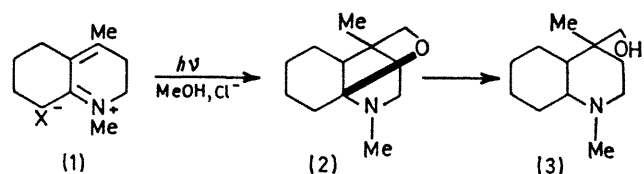
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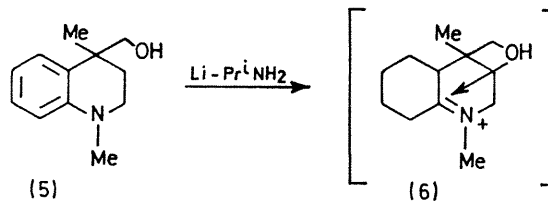
Summary Photoaddition of methanol to 1,4-dimethyl-2,3,5,6,7,8-hexahydroquinolinium perchlorate (**1**) in a chloride dependent reaction gave 7,10-dimethyl-10-aza-11-oxatricyclo[5,3,2,0^{1,6}]dodecane (**2**).

In view of the recent interest¹ in photoadditions of alcohols to C=C, C=N, and C=N< linkages, we report the photocycloaddition of methanol to the conjugated iminium salt (**1**). Irradiation of a solution of (**1a**) in MeOH-HCl(10⁻²M; λ_{\max} 303 nm) at 313.0 nm with a medium-pressure lamp resulted in the disappearance of the chromophore in 24 h. The major product (70%) after neutralisation, isolated by preparative g.l.c., was identified as the tricyclic compound (**2**), an oil, δ (CCl₄) 3.57 br (2H, s, OCH₂), 2.10 (3H, s, NMe), and 0.95 p.p.m. (3H, s, CMe), *m/e* 195. The structure was unequivocally assigned by reductive cleavage (NaBH₄-THF) to the alcohol (**3**) (*m/e* 197) and by synthesis from (**5**).[†]

No reaction occurs with either (**1a**) or (**1b**) unless chloride ion is present, either as HCl or LiCl; a minimum of 5.0 equiv. of chloride ion was necessary for the photoaddition



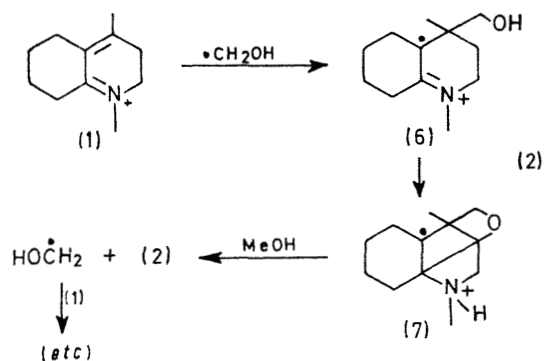
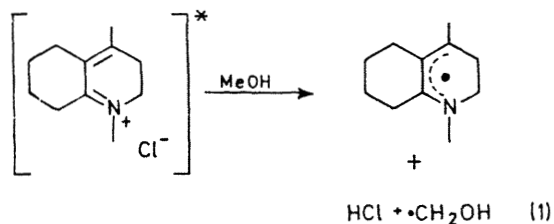
a; X = ClO₄
b; X = Br⁻
c; X = Cl⁻



to proceed. A previous report² described the photoaddition

[†] Details of this reaction will be reported later.

of methanol to 3,6-dichloropyridazine catalysed by hydrogen



chloride, but the reaction also proceeded in its absence, unlike the present case.

Preparation of the tricyclic base (2) from (1a) was also accomplished thermally with methanolic benzoyl peroxide which is known to produce hydroxymethyl radicals.³ These data have led us to suggest a pathway leading to (2) [equations (1) and (2)].

The exact mechanism by which the photoexcited state of (1) gives rise to hydroxymethyl radicals is still obscure and will be discussed fully later. The hydroxymethyl radical [equation (1)] adds to the unexcited dihydropyridinium salt producing the new radical (6) [equation (2)]. This radical then undergoes a rapid intramolecular addition to the electrophilic iminium bond giving (7) which abstracts hydrogen from the solvent to give the product (2). When the photoreaction was performed in MeOD with deuterium chloride, there was no detectable incorporation of deuterium into (2), thus confirming that the ring-junction hydrogen originated from C-H homolytic cleavage rather than O-H rupture or protonation by hydrochloric acid. The delocalised radical shown in equation (1) is currently assumed to be responsible for the reduced quinolines observed (*ca.* 30%) as side products.

The support of the National Institutes of Health, U.S. Public Health Service, is gratefully acknowledged.

(Received, March 29th, 1971; Com. 438.)

¹ S. T. Reid, *Adv. Heterocyclic Chem.*, 1969, **11**, 57; J. A. Marshall, *Accounts Chem. Res.*, 1969, **33**; P. J. Kropp, *J. Amer. Chem. Soc.* 1969, **91**, 5783; F. R. Stermitz, C. C. Wei, and C. M. O'Donnell, *ibid.*, 1970, **92**, 2745; A. Padwa, W. Bergmark, and D. Pashayan, *ibid.* 1969, **91**, 2653.

² T. Tsuchiya, H. Arai, and H. Igeta, *Tetrahedron Letters*, 1970, 3839.

³ C. Walling, "Free Radicals in Solution," Wiley, New York, 1957, p. 479.