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Photoreaction of 5-Bromo-1,3-dimethyluracil with 1,4-Xylene. The Effect of Acid

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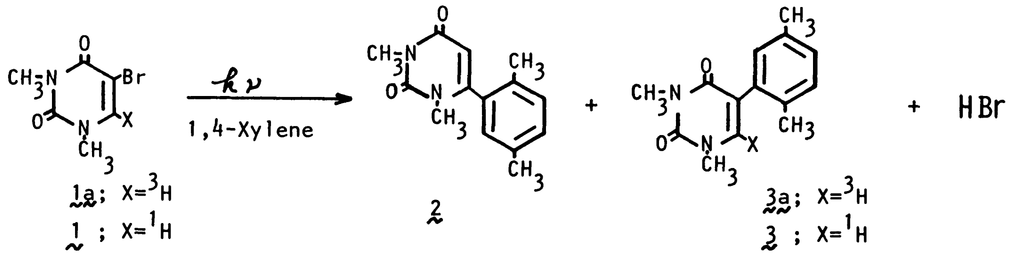
The photoreaction of 5-bromo-1,3-dimethyluracil in 1,4-xylene solution yields a mixture of 5- and 6-aryl substituted uracils. The 5-isomer is formed first and is followed by the 6-isomer, the latter being the product from protonated uracil. In the presence of initially added acid (HBr and trifluoroacetic acid) both isomers are formed simultaneously.

The photochemistry of uracil and its 5-bromo derivative has been studied from the biological and photochemical points of view.1) In a previous communication2) we reported that 6-aryluracils were produced together with the expected 5-aryluracils upon irradiation of 5-bromo-1,3-dimethyluracil (**1**) in solutions of various substituted benzenes. The mechanism for the formation of the 6-isomer was unclear. A benzyne-like mechanism3) is readily eliminated by the photoreaction of 6-tritium labeled **1** (**1a**) in 1,4-xylene (xylene) solution. Almost no radioactivity was detected in the isolated 6-isomer (**2**), while the 5-isomer (**3a**) retained almost all of the activity. In this paper we report our findings that the unexpected 6-aryluracils result from the photoreaction of protonated **1**.



A rate study of the photoreaction of **1** in xylene4) showed that the production of **2** began after the formation of **3** (Fig. 1). This indicated that **2** may have resulted from the isomerization of **3**, or that some byproduct of the initial reaction influenced the formation of **2**. However the photolysis of pure **3** in xylene solution did not yield **2**. We then examined the effect of other products of the reaction and found that HBr was essential for the formation of **2**.

In the presence of initially added HBr, the time lag disappeared and both **2** and **3** formed simultaneously resulting in a final ratio of **2**/**3** significantly higher than in the absence of added acid (ca. 1.1 vs. 0.34 after 10 h) (Fig. 2). The effect of HBr on the formation of **2** was completely blocked in the presence of base (pyridine, aq. K_2CO_3). Trifluoroacetic acid (TFA) (0.5 M/xylene) also accelerated the formation of 2, but less effectively (2/3 = 0.56-0.65 after 10 h).

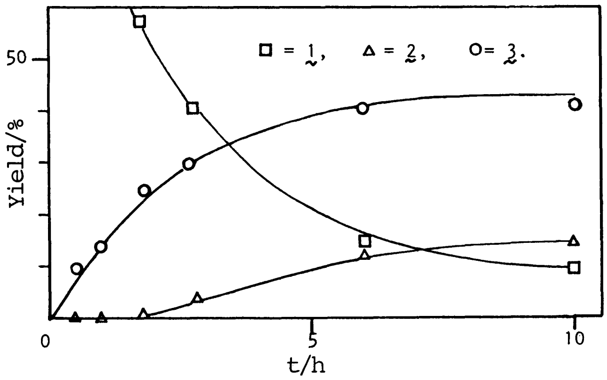


Fig. 1. Photoreaction of 1 in xylene.

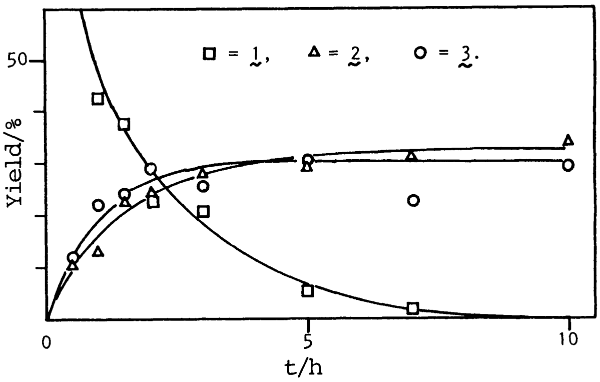


Fig. 2. Photoreaction of 1 in xylene in the presence of HBr.

The UV spectrum of 1 (0.13 mM) in cyclohexane containing TFA (0.15 M) and xylene (13 mM) shifted 5 nm to the red (λ_{max} 278 nm to 283 nm), but did not show a new absorption,[5] while no change was observed in methanol. These results are in agreement with the finding that the ratio of 2/3 = 0.2 in cyclohexane approached to zero in methanol (Table 1).

Table 1. Solvent effect on the photoreaction of 1 with xylene[a]

1 (mg)	Solvent	Yield of the Product/%				Recovered
		2	3	4[b]	Σ[c]	1/%
2.5	Cyclohexane	7.3	36	12	61	10
5	Ether	0.6	23	31	75	27
5	Methanol	0.0	52	11	68	7

a) 1 was irradiated in a mixture of xylene (2 ml) and a solvent (8 ml) for 10 h. b) 1,3-Dimethyluracil. c) Total yield (2+3+4) based on 1 consumed.

The formation of 2 was completely suppressed by the addition of piperylene in the reaction with xylene; this suggested that the 6-substituted uracil 2 arose from the photolysis of protonated 1[6] probably via a triplet excited state.[7]

References

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2) K. Seki, Y. Bando, and K. Ohkura, Chem. Lett., 1986, 195.
3) R. D. Youssefyeh and L. Lichtenberg, J. Chem. Soc., Perkin Trans. 1, 1974, 2649.
4) Photoreaction of 1 (5 mg) in xylene (5 ml) was carried out in degassed sealed tube (Pyrex) by external irradiation with a 500 W high pressure mercury lamp (Eikosha). The analysis of the reaction mixture was performed by reverse-phase HPLC.
5) M. Tada, H. Saiki, K. Miura, and H. Shinozaki, Bull. Chem. Soc. Jpn., 49, 1666 (1976).
6) The mechanism for the formation of 2 from protonated 1 remains uncertain, but in view of the isomer distributions of 6-isomers obtained by the reaction of 1 with toluene and anisole in which the meta isomers were formed predominantly,[2] it would be supposed that 2 was produced by the electrophilic attack of protonated 1 to the excited xylene followed by dehydrobromination.[8]
7) S. Ito, I. Saito, and T. Matsuura, J. Am. Chem. Soc., 102, 7535 (1980).
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