

PHOTOCYCLODEHYDROHALOGENATION OF 5-IODO-6-PHENOXY-1,3-DIMETHYL-
URACIL AND 5-IODO-6-THIO-PHENYL-1,3-DIMETHYLURACIL

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The photocyclodehydrohalogenation to give both five- and six-membered ring closure has been studied¹. We have examined the photochemical behavior of 5-iodo-6-phenoxy-1,3-dimethyluracil (1) and 5-iodo-6-thiophenyl-1,3-dimethyluracil (8), in benzene and acetonitrile in an effort to examine the requirements for generation of five-membered rings in this type of systems. The iodo(I)³ (75%) [(m.p. 128°C; nmr (CDCl₃) δ 3.36 (s, NMe, 3H), 3.42 (s, NMe, 3H), 6.88-7.55 (m, aromatic H, 5H)] was synthesized by replacement of the chloro of 6-chloro-1,3-dimethyluracil (2)² by phenoxy group using sodium phenoxide followed by iodination with mercuric acetate and iodine².

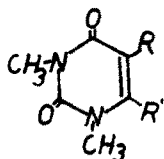
Irradiation of (I) in benzene for 1½ hr at room temperature in a cylindrical quartz cell utilizing the light from a Hanovia 100 watts high pressure mercury lamp, led to a mixture of products from which the pyrimidobenzofuran (3)² (1%) [(m.p. 185-6°C; nmr (CCl₄) δ 3.42 (s, NMe, 3H), 3.62 (s, NMe, 3H), 7.30 (m, aromatic 3H), 7.91 (m, aromatic H, 1H)], 6-ortho-biphenyloxy-1,3-dimethyluracil³ (4) (15%) [(m.p. 154-5°C; nmr (CCl₄) δ 3.11 (s, NMe, 3H), 3.26 (s, NMe, 3H), 6.52 (s, C₅H, 1H), 7.26 (m, aromatic H, 9H)], 5-phenyl-6-phenoxy-1,3-dimethyluracil³ (5) [(m.p. 119-20°C; nmr (CDCl₃) δ 3.38 and 3.44 (s, NMe, 6H), 6.7-7.4 (m, aromatic H, 10H)], biphenyl ether⁴, and 2-hydroxybiphenyl⁵ were isolated.

The compounds (4) and (5) were further synthesized and identified by direct replacement of the 6-chloro of (2) and (6) with ortho-biphenoxy and phenoxy group, respectively.

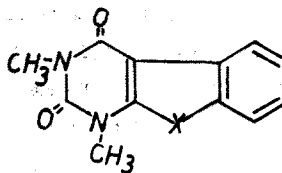
Photolysis of (I) in acetonitrile led to 3 (1%) and 6-phenoxy-1,3-dimethyluracil³ (7) (14%) [(m.p. 107-8°C; nmr (CCl₄) δ 3.20 (s, NMe, 3H), 3.48 (s, NMe, 3H), 4.55 (s, C₅H, 1H), 7-7.6 (m, aromatic H, 1H)].

Similar irradiation of 5-iodo-6-thiophenyl-1,3-dimethyluracil³ (8) [(m.p. 185-6°C, nmr (CDCl₃) δ 3.42 (s, NMe, 3H), 3.55 (s, NMe, 3H), 7.30 (s, aromatic H, 5H)], which was synthesized by the same procedure as for (1) using thiophenol instead of phenol, in acetonitrile led to 6-thiophenyl-1,3-dimethyluracil⁶ (7) [(m.p. 129-30°C;

nmr (CDCl_3) δ 3.28 (s, NMe, 3H), 3.55 (s, NMe, 3H), 4.95 (s, C_5H , 1H), 7.42 (s, aromatic H, 5H), and the pyrimidobenzo[thiophene] 6(10) (42%) [m.p. 185-7°C; nmr (CCl_4) δ 3.34 (s, NMe, 3H), 3.50 (s, NMe, 3H), 7.2-7.76 (m, aromatic H, 3H), 8.48 (m, aromatic H, 1H); mass spectrum m/e 246 (M^+)].



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| 1. R = I, R' = $\text{C}_6\text{H}_5\text{O}$ | 6. R = C_6H_5 R' = Cl | 3. X = O |
| 2. R = H, R' = Cl | 7. R = H, R' = $\text{C}_6\text{H}_5\text{O}$ | 10. X = S |
| 4. R = H, R' = ortho- $\text{C}_6\text{H}_4\text{O}$ | 8. R = I, R' = $\text{C}_6\text{H}_5\text{S}$ | |
| 5. R = C_6H_5 , R' = $\text{C}_6\text{H}_5\text{O}$ | 9. R = H, R' = $\text{C}_6\text{H}_5\text{S}$ | |



The formation of the products isolated serves as an evidence for a free radical mechanism. The biphenyloxyuracil(4) was probably formed by intramolecular hydrogen abstraction involving conversion of 6-phenoxy-1, 3-dimethyl-5-uracil radical to its isomeric phenoxy radical followed by the interaction of the latter radical with the solvent benzene. The isolation of diphenyl ether and 2-hydroxybiphenyl is perhaps an indication of 1,3dimethyl-5,6-dehydrouracil formation. However, under identical reaction condition no Diels-Alder adduct was observed when tetracyclone was present.

Efforts are being made in order to develop further and to extend this novel method of synthesis of pyrimidobenzo-furans and thiophenes to other related systems and to understand the reaction mechanism.

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