Photolysis of 5,6-Iodo-1,3-dimethyluracil in Benzene and in Furan

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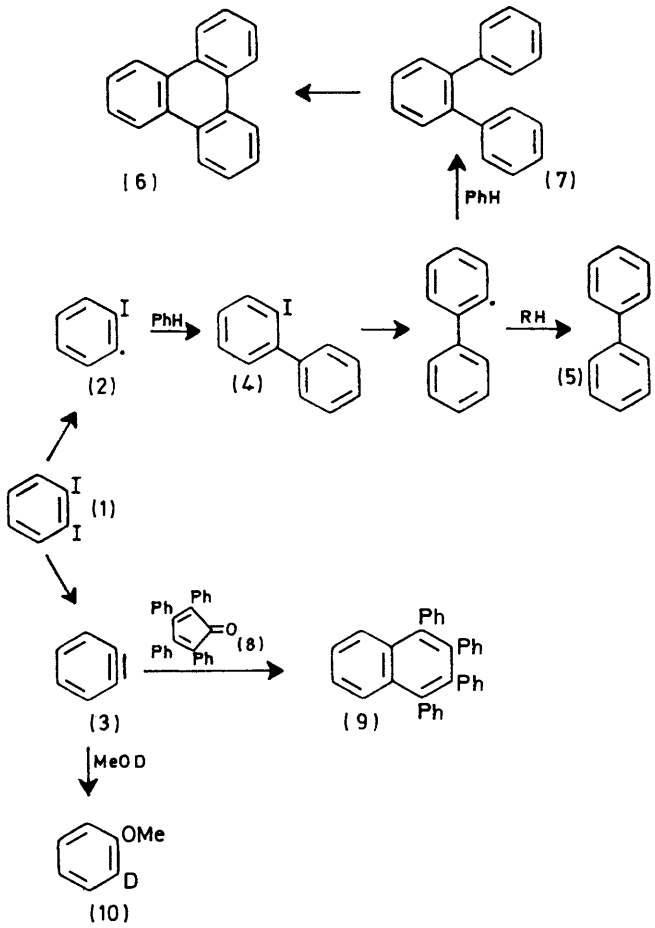
In contrast to 1,2-di-iodobenzene, photolysis of 5,6-di-iodo-1,3-dimethyluracil in benzene and in furan rapidly gives products derived from a radical intermediate and none derived from the corresponding pyrimidyne. 5-Iodo-1,3-dimethyluracil radical is believed to be the precursor of all the identified products. The scope and mechanism of these photoreactions are discussed.

It has been reported that photolysis of 1,2-di-iodobenzene (1) gives products derived both from 2-iodophenyl radical (2) and from benzene (3). Irradiation [1] in benzene gave mainly 2-iodobiphenyl (4) and small amounts of biphenyl (5) and triphenylene (6). Recent work has clearly demonstrated that triphenylene (6) is formed by cyclodehydrogenation of *o*-terphenyl [2] (7). Performance of the irradiation in the presence of tetracyclone (8) led to 1,2,3,4-tetraphenylnaphthalene (9), which can be interpreted as arising through the expected Diels–Alder reaction with benzyne (3). Further evidence for generation of benzyne (3) was obtained [3] by performing the photolysis in deuteriomethanol. Mass spectral analysis of the anisole formed showed it to consist mostly of monodeuterioanisole (10). A free-radical pathway to benzyne, involving the elimination of an iodine atom from 2-iodophenyl radical or a simultaneous elimination of both iodine atoms from 1,2-di-iodobenzene (1), has been proposed.[1,3] However, no clear decision as to the relative merits of these two schemes was reached. Photolysis of other di- and tri-iodobenzene derivatives in benzene, presumably by a free-radical pathway, gives rise to the expected phenylation products. For example, irradiation of 2,4,6-tri-iodophenol in benzene leads to 2,4,6-triphenylphenol.[4]

We therefore considered photolysis of 5,6-di-iodopyrimidines as a potential route to pyrimidynes. (Evidence for the occurrence of pyrimidynes in the amination of both 6- and 5-bromo-pyrimidines has been presented.[5]) In contrast to 1,2-di-iodobenzene, however, the strengths of the two carbon–iodine bonds in 5,6-di-iodopyrimidines are not the same, and a simultaneous removal of the two iodine atoms is thus unlikely. Generation of a pyrimidyne by loss of the second iodine atom from the radical formed from irradiation of



[1] J. A. Kampmeier and A. B. Rubin, *J. Amer. Chem. Soc.*, 1962, **84**, 3787.

[2] N. Kharasch, T. G. Alston, H. B. Lewis, and W. Wolf, *Chem. Comm.*, 1965, 242.

[3] R. K. Sharma and N. Kharasch, *Angew. Chem. Internat. Edn.*, 1968, **7**, 36.

[4] N. Kharasch, W. Wolf, T. J. Erpelding, P. G. Naylor, and L. Tokes, *Chem. and Ind.*, 1962, 1720.

[5] H. C. van der Plas, P. Smit, and A. Koudijs, *Tetrahedron Letters*, 1968, 9; R. Promel, A. Cardon, M. Daniel, G. Jaquer, and A. Vandermissen, *ibid.*, p. 3067; T. J. Schwan and H. Tieckelmann, *J. Org. Chem.*, 1964, **29**, 941.

a 5,6-di-iodopyrimidine must therefore compete with the other possible radical reactions, such as addition or hydrogen atom abstraction.

We decided to study the photolysis of a 5,6-di-iodopyrimidine in benzene and in furan in order to investigate whether pyrimidyne is an intermediate. 5,6-Di-iodo-1,3-dimethyluracil [6] (11) was chosen as a suitable model because of its solubility in these solvents and the ease of handling of its photoproducts. Reactions were conducted near room temperature in a cylindrical quartz cell or quartz tube utilizing the light from a Hanovia 100 W high-pressure mercury lamp. Free iodine was formed readily in all photolyses and usually hindered further reaction, presumably by converting the reaction intermediate into starting material.† It was therefore necessary, in some cases, to maintain the free iodine concentration at a low level by extraction at intervals with sodium hydrogen sulphite.

Irradiation of compound (11) in furan for 30 min with extraction of iodine led to 6-(2-furyl)-5-iodo-1,3-dimethyluracil (13) and 6-(2-furyl)-1,3-dimethyluracil (15). The structure of (13) was established by its reduction with zinc–hydrochloric acid to (15). This in turn was synthesized by irradiation of 6-iodo-1,3-dimethyluracil (16) in furan. To distinguish between 5- and 6-(2-furyl)-1,3-dimethyluracil, the 5-(2-furyl) isomer (17) was also prepared, from irradiation of 5-iodo-1,3-dimethyluracil (18) in furan. The n.m.r. spectral data of compounds (13), (15), and (17) are compared in the Table. In all substances examined [8] the 6-H signal occurs at lower field (δ 7—8) than the 5-H signal (δ 5·5—7). The splitting patterns of the furan protons are as expected for 2-substituted furans.

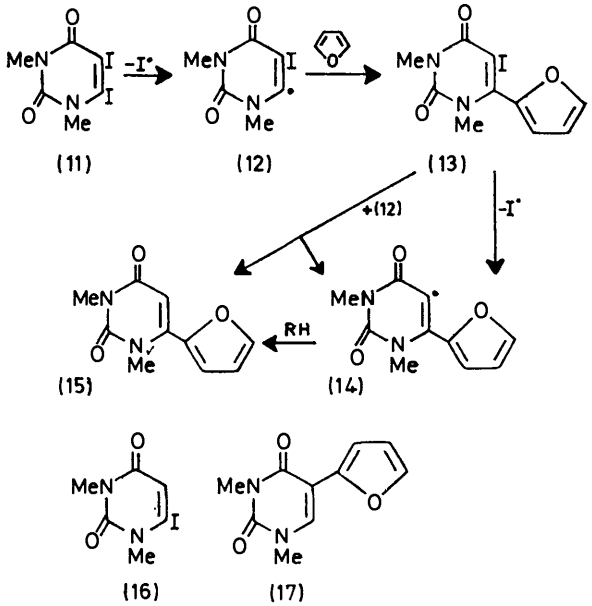
The isolation of 6-(2-furyl)-5-iodo-1,3-dimethyluracil (13) is evidence for a free-radical mechanism, and, along with the absence of the 5-(2-furyl)-6-iodo-isomer, indicates the preferred cleavage of the C(6)–I rather than the C(5)–I bond. 6-(2-Furyl)-1,3-dimethyluracil (15) is most probably obtained from (13) by way of the radical (14), formed either by direct C(5)–I bond scission or (preferably) by a bimolecular disproportionation reaction involving (13) and (12), since no 6-(2-furyl)-1,3-dimethyluracil (15) was obtained when the reaction mixture was diluted six-fold with furan. In contrast to 1,2-di-iodo-benzene, photolysis of 5,6-di-iodo-1,3-dimethyluracil in the presence of tetracyclone gave no pyrimidyne Diels–Alder adduct.

In a similar manner, from photolysis of 5,6-di-iodo-1,3-dimethyluracil (11) in benzene were isolated 1,3-dimethyluracil (22), 1,3-dimethyl-5-phenyluracil (23), 1,3-dimethyl-6-phenyluracil (28), 6-(biphenyl-2-yl)-1,3-dimethyluracil (30), and 2,4-dimethyldibenzo[*f*,*h*]quinazoline-1,3-dione (31).[9] Irradiation of (11) in benzene containing an equimolecular amount of tetracyclone under the same conditions failed to give any Diels–Alder adduct. The observed products again suggest the formation of free radical intermediates, but no pyrimidyne. The 5-iodo-1,3-dimethyluracil radical (19) is probably a precursor of all the products detected. The 1,3-dimethyluracil radicals (21) generated by way of the radicals (18) and (19) react by either hydrogen abstraction or free-radical substitution into benzene leading to compounds (22) and (23), respectively. Compound (23) was identified by spectroscopic methods

N.m.r. spectral data of substituted 1,3-dimethyluracils in $CDCl_3$ (δ values; *J* in Hz)

Substance	1-Me	3-Me	6-H	5-H	Furan H_a	Furan H_b	Furan H_c	Ph or C_6H_4
(13)	3·54 (s)	3·22 (s)			7·63 (d, J_{ab} 3·5)	6·57 (q, J_{ba} 3·5, J_{bc} 2)	6·77 (d, J_{cb} 2)	
(15)	3·50 (s)	3·37 (s)		6·9 (s)	7·60 (d, *J* 3·5)	6·52 (q, *J* 3·5, *J* 2)	6·77 (d, *J* 2)	
(17)	3·50 (s)	3·42 (s)	7·7 (s)		7·37 (d, *J* 3·5)	6·47 (q, *J* 3·5, *J* 2)	7·07 (d, *J* 2)	
(16)	3·65 (s)	3·29 (s)		6·45 (s)				
(18)	3·40 (s)		7·57 (s)					
(23)	3·45 (s)	3·40 (s)	7·61 (s)					7·4 (m)
(28)	3·38 (s)	3·21 (s)		5·67 (s)				7·38 (m)
(28) *	3·28 (s)	3·14 (s)		5·49 (s)				7·38 (m)
(30)	3·36 (s)	3·06 (s)		5·63 (s)				7·1 (m)

* In CCl_4.



† 1,2-Di-iodobenzene has been obtained [7] from the decomposition of *N*-(2-iodophenyl)-*N*-nitrosobenzamide.

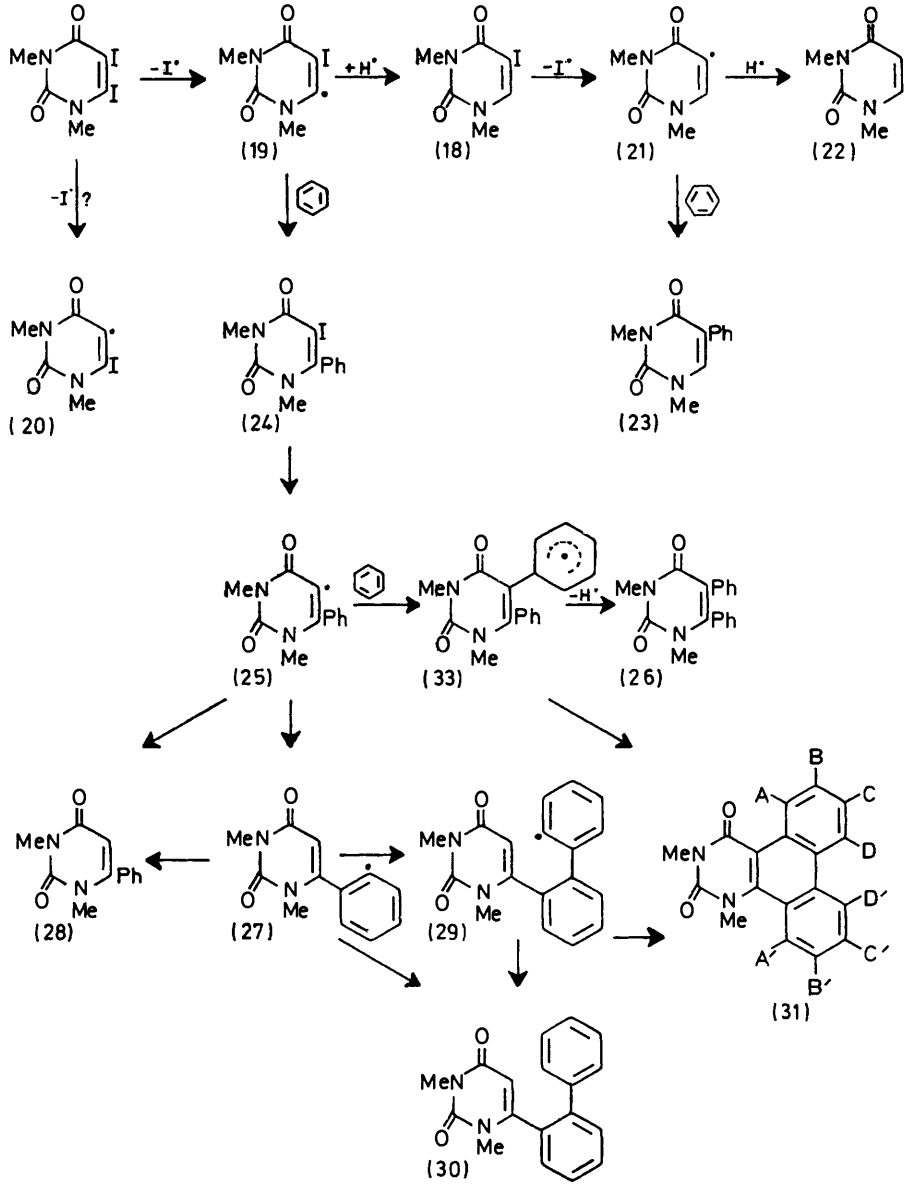
[6] W. Pfleiderer and H. Deiss, *Israel J. Chem.*, 1968, 603.

[7] J. A. Kampmeier and A. B. Rubin, *Tetrahedron Letters*, 1966, 2853.

[8] N.m.r. data for other 5- and 6-substituted 1,3-dimethyluracils will be published at a later date; D. J. Brown, 'The Pyrimidines,' Supplement I, Interscience, New York, 1970, p. 386.

[9] R. D. Youssefyeh and M. Weisz, *J. Amer. Chem. Soc.*, 1974, **96**, 315.

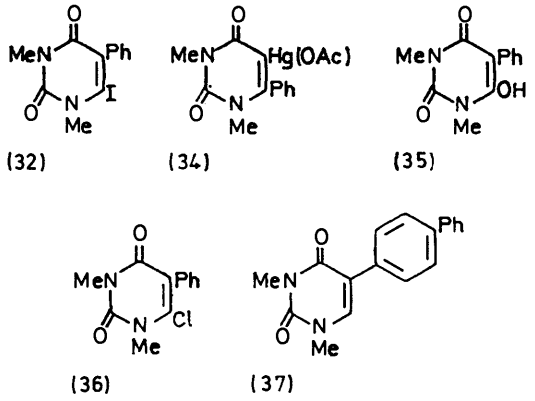
and by comparison with material obtained from reduction of 6-iodo-1,3-dimethyl-5-phenyluracil (32) with zinc–hydrochloric acid and from irradiation of 5-iodo-1,3-dimethyluracil (18) in benzene. The absence of 5-biphenyl-4-yl-1,3-dimethyluracil (37) and the detection



of 5-iodo-1,3-dimethyluracil (18) among the products from irradiation of (11) in benzene, which again is an indication of the preferred C-6 rather than C-5 cleavage, implies that the radical (19) plays a major role in the formation of (30) *via* the radical (27), generated from (25) by intramolecular hydrogen abstraction. The radical (27) may undergo photoreduction, abstracting hydrogen from the solvent, to give (28), or undergo intermolecular reaction with solvent benzene to yield (30). 1,3-Dimethyl-6-phenyluracil (28) was also obtained from photolysis of 6-iodo-1,3-dimethyluracil (16) in benzene and by reduction of 5-iodo-1,3-dimethyl-6-phenyluracil (24) with zinc–hydrochloric acid. Compound (30) was identified on the basis of its spectroscopic (particularly n.m.r.) data. To establish which species were the precursors of (31), the two isomers (26) and (30) were irradiated under the same conditions. Compound (30) gave (31), but (26) remained unchanged. This rules out (26) as an intermediate on the way to (31), but not the radical (33), which may be regarded as the precursor of (26).

5-Iodo-1,3-dimethyl-6-phenyluracil (24) and its isomer 6-iodo-1,3-dimethyl-5-phenyluracil (32) were synthesized by an unambiguous method in order to examine their photoreactions under the same conditions in benzene. Compound (24), as expected, gave a mixture of 1,3-dimethyl-5,6-diphenyluracil (26), 6-(biphenyl-2-yl)-1,3-dimethyluracil (30), and the dibenzoquinazoline (31); its isomer (32) gave 1,3-dimethyl-5-phenyluracil (23) and

the dibenzoquinazoline (31). This illustrates that if 6-iodo-1,3-dimethyl-5-phenyluracil (32) were formed as an intermediate in the irradiation of 5,6-di-iodo-1,3-dimethyluracil, it would lead to the dibenzoquinazoline

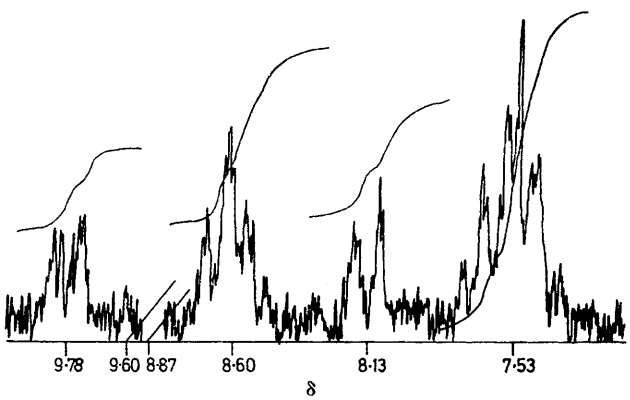


(32) (34) (35)

(36) (37)

(31). However, its intermediacy is questionable since it requires the radical (20) as precursor.

The structure of (31) was confirmed by its n.m.r. spectrum, a part of which is shown in the Figure. A



Part of the n.m.r. spectrum of compound (31)

one-proton signal at δ 9·78 (dd, J_{AB} 8·2, J_{AC} 2·5 Hz) is due to H_A, a two-proton signal at 8·40—8·73 (m) to $H_D + H_{D'}$, a one-proton signal at 8·13 (dd) to $H_{A'}$, and a four-proton signal at 7·46—7·94 (m) to $H_C + H_B + H_{C'} + H_{B'}$. The signals at δ 8·40—8·73 appear as a triplet at 100 MHz, but as a multiplet at 60 MHz. A genuine triplet would show no such change and the signal is therefore believed to be a combination of two double doublets due to H_D and $H_{D'}$.

EXPERIMENTAL

Compounds were irradiated near room temperature in a cylindrical quartz cell under nitrogen with a Hanovia 100 W high-pressure mercury-vapour lamp. Furan, benzene, and acetonitrile were distilled and dried before use. M.p.s were determined with a Thomas-Hoover capillary apparatus. I.r. spectra were measured with a Perkin-Elmer 137 Infracord, and u.v. spectra with a Unicam SP 800 spectrophotometer; mass spectra were obtained with a Varian MAT CH-5, and n.m.r. spectra with a JEOL C-60H high resolution 60 MHz spectrometer (tetramethylsilane as internal standard). T.l.c. was carried out with plates coated with Kieselgel PF 254 FM (Merck); spots were located by u.v. illumination.

6-Iodo-1,3-dimethyluracil (16).—The 6-iodo-compound (16), prepared by the method of Pfleiderer *et al.*,[6,10] had m.p. 171—173° (lit.,[6,10] 174—175°); *m/e* 266 (M^+), 209 ($M - CH_3NCO$), and 82 (209 − I); δ [$(CD_3)_2SO$] 3·08 (3H, s, NMe), 3·51 (3H, s, NMe), and 6·40 (1H, s, 5-H); δ ($CDCl_3$) 3·29 (s), 3·65 (s), and 6·45 (s); $\nu_{max.}$ (KBr) 680, 745, 845, 950, 1025, 1400, 1620, and 1670 cm^{-1}.

5,6-Di-iodo-1,3-dimethyluracil (11).—The di-iodo-compound (11) synthesized by way of (16) as described by Pfleiderer *et al.*,[6] had m.p. 212—213° (lit.,[6] 213—215°); *m/e* 392 (M^+), 335 ($M - CH_3NCO$), 208 (335 − I), and 81 (208 − I); δ ($CDCl_3$) 3·44 (3H, s, NMe) and 3·95 (3H, s, NMe); $\nu_{max.}$ (KBr) 750, 1360, 1425, 1525, 1625, and 1675 cm^{-1}.

5-Iodo-1,3-dimethyluracil (18).—A mixture of 1,3-dimethyluracil (22) (200 mg) and mercury(II) acetate (452 mg) in ethanol (50 ml) was stirred until the mercury derivative of (22) precipitated. An excess of iodine was added and the mixture was refluxed overnight. Mercury(II) iodide was filtered off and the solution was concentrated, washed with concentrated potassium iodide solution, and filtered to give compound (18) (140 mg), m.p. 124—125° (from methanol); *m/e* 266 (M^+), 209 ($M - CH_3NCO$), and 82 (209 − I); δ [$(CD_3)_2SO$] 3·57 (6H, s, NMe) and 8·20 (1H, s, 6-H); δ ($CDCl_3$) 3·40 (6H, s, NMe) and 7·57 (1H, s, 6-H); $\nu_{max.}$ (KBr) 750, 1625, and 1700 cm^{-1}.

1,3-Dimethyl-6-phenyluracil (28).—Compound (28), synthesized by the method described by Burckhalder and Scarborough,[11] had m.p. 121—122° (lit.,[11] 121—122°); *m/e* 216 (M^+), 215 (M − H), 159 ($M - CH_3NCO$), 158 (159 − H), 131 (159 − CO), 130 (131 − H), 118 (159 − C_2HO), and 82 (159 − Ph); δ (CCl_4) 3·14 (3H, s, NMe), 3·28 (3H, s, Me), 5·49 (1H, s, 5-H), and 7·38 (5H, s, aromatic); $\lambda_{max.}$ (EtOH) 273 nm (ε 7128); $\nu_{max.}$ (KBr) 695, 705, 754, 770, 832, 1000, 1200, 1450, 1625, and 1690 cm^{-1}.

Reaction of Compound (28) *with Mercury*(II) *Acetate.*—A mixture of compound (28) (500 mg) and of mercury(II) acetate (800 mg) in ethanol (150 ml) was stirred at 50 °C overnight to give a mixture (1·1 g) of bis-(1,3-dimethyl-6-phenyluracil-5-yl)mercury and 1,3-dimethyl-6-phenyluracil-5-ylmercury acetate (34). Separated by t.l.c. (CH_2Cl_2), the acetate (34) showed δ ($CDCl_3$) 2·0 (3H, s, CH_3), 3·23 (3H, s NMe), 3·44 (3H, s, NMe), and 7·52 (5H, m, aromatic)

5-Iodo-1,3-dimethyl-6-phenyluracil (24).—A mixture of the mercury acetate (34) (100 mg) and *N*-iodosuccinimide (200 mg) in ethanol (15 ml) was refluxed for 30 h. Removal of solvent, extraction of mercury(II) iodide with concentrated potassium iodide solution, and filtration gave compound (24) (52 mg), m.p. 150—151° (from ether); δ ($CDCl_3$) 3·16 (3H, s, NMe), 3·47 (3H, s, NMe), and 7·25 and 7·55 (5H, aromatic); *m/e* 342 (M^+), 285 ($M - CH_3NCO$), 214 (M − HI), 157 (214 − CH_3NCO), 129 (157 − CO), and 118 (285 − C_2IO).

Reduction of the 5-Iodouracil (24).—A mixture of compound (24) (20 mg), ethanol (8 ml), N-hydrochloric acid (1·50 ml), and zinc dust (80 mg) was refluxed for 2 h. Solvent was then removed, and the residue was diluted

[10] W. Pfleiderer and K. H. Schundehutte, *Annalen*, 1958, **612**, 158.

[11] T. B. Johnson and E. H. Hemingway, *J. Amer. Chem. Soc.*, 1915, **37**, 378; J. H. Burckhalter and H. C. Scarborough, *J. Amer. Pharm. Assoc.*, 1955, **44**, 545.

with water, neutralized with 10% Na_2CO_3 solution, and extracted with dichloromethane. The product, m.p. 148—150° was identical (u.v., n.m.r., and mass spectra) with compound (28).

1,3-*Dimethyl*-5-*phenylbarbituric Acid* [12] (35).—Sodium (27 g) was dissolved in absolute ethanol (350 ml), *NN*-dimethylurea (33 g) and diethyl phenylmalonate (93 mg) were added, and the mixture was refluxed for 12 h. Ethanol was then removed, and the mixture was diluted with water and extracted with ether. The aqueous solution was acidified with concentrated hydrochloric acid, cooled, and filtered. The product obtained was crystallized from water–ethanol to give compound (35) (3·5 g), m.p. 136° (lit.,[12] 141—142°); δ ($CDCl_3$) 3·28 (6H, s, 2 NMe), 4·6 (1H, s, OH, exchanged in D_2O), and 7·25 (5H, m, aromatic).

6-*Chloro*-1,3-*dimethyl*-5-*phenyluracil* [12] (36).—The hydroxypyrimidine (35) (1 g), phosphoric trichloride (5 ml), and water (3 drops) were refluxed for 5 h. The excess of phosphoric trichloride was distilled off; addition of ice–water and extraction with ether, drying ($MgSO_4$) and evaporation then gave an oily residue which was chromatographed over alumina (50 g). Elution with 50% ether–petroleum gave compound (36) (410 mg), m.p. 131—133° (from ether) (lit.,[12] 134—136°); δ (CCl_4) 3·30 (3H, s, NMe), 3·59 (3H, s, NMe), and 7·22 (5H, m, aromatic).

6-*Iodo*-1,3-*dimethyl*-5-*phenyluracil* (32).—A solution of compound (35) (200 mg) in 66% hydroiodic acid (5 ml) was stirred for 24 h. The mixture was basified with sodium carbonate and then extracted with dichloromethane; the extract was washed with a solution of sodium thiosulphate, dried, and evaporated to give compound (32) (180 mg), m.p. 187—188° (from dichloromethane–petroleum); δ ($CDCl_3$) 3·38 (3H, s, NMe), 3·80 (3H, s, NMe), and 7·32 (5H, m, aromatic); *m/e* 342 (M^+), 158 [M − (I + CH_3NCO)], 130 (158 − CO), and 77 (130 − CH_3CN).

Irradiation of 5,6-*Di-iodo*-1,3-*dimethyluracil* (11) *in Furan*.—(*A*) Irradiation of compound (11) (100 mg) in furan (25 ml) for 30 min with periodic extraction of free iodine by sodium hydrogen sulphite, followed by evaporation, and t.l.c. of the residue, led to (i) 6-(2-furyl)-1,3-dimethyluracil (15) (7·9 mg, 15%), m.p. 119—120°; R_F (ether) 0·60; *m/e* 206 (M^+), 149 (206 − CH_3NCO), 121 (149 − CO), and 108 (149 − C_2HO); δ ($CDCl_3$) 3·37 (3H, s, NMe), 3·5 (3H, s, NMe), 6·9 (1H, s, 5-H), 7·6 (1H, d), 6·25 (1H, q), and 6·77 (1H, d); $\lambda_{max.}$ (EtOH) 302 (ε 14,162), 273 (10,042), and 265 nm (9656); (ii) starting material (60 mg, 60%), R_F (ether) 0·68; and (iii) 6-(2-furyl)-5-iodo-1,3-dimethyluracil (13) (20 mg, 23%), m.p. 158°; R_F (ether) 0·71; *m/e* 332 (M^+), 275 (M − CH_3NCO), 108 (275 − C_2IO), 148 (275 − I), and 120 (148 − CO); $\lambda_{max.}$ (EtOH) 302 nm (ε 6774).

(*B*) Irradiation of (11) (200 mg) in furan (300 ml) under the same conditions led to compound (13) (34·5 mg, 35%).

Reduction of Compound (13).—To a solution of compound (13) (20 mg) in absolute ethanol (7 ml) were added concentrated hydrochloric acid (1·5 ml) and zinc dust (80 mg), and the mixture was refluxed for 1 h. Ethanol was then removed and the residue was neutralized (10% $NaHCO_3$) and extracted with dichloromethane. The organic layer was washed with water, dried, and evaporated to give 6-(2-furyl)-1,3-dimethyluracil (15) (6 mg).

Irradiation of 6-*Iodo*-1,3-*dimethyluracil* (16) *in Furan*.—A solution of compound (16) (100 mg) in furan (100 ml) was irradiated for 1 h with periodic extraction with sodium sulphite solution. Work-up as before gave 6-(2-furyl)-1,3-dimethyluracil (15) (35 mg, 45%).

Irradiation of 5-*Iodo*-1,3-*dimethyluracil* (18) *in Furan*.—Compound (18) (100 mg) in furan (100 ml) was irradiated for 1 h with periodic extraction with sodium hydrogen sulphite solution. After work-up as before, t.l.c. gave (i) 5-(2-furyl)-1,3-dimethyluracil (17) (23 mg, 30%), m.p. 175°; R_F (ether) 0·81; *m/e* 206 (M^+), 149 (M − CH_3NCO), 121 (149 − CO), and 108 (149 − CH_3CN); $\lambda_{max.}$ (EtOH) 315 (ε 7004) and 252 nm (7931); (ii) starting material (35 mg, 35%), m.p. 124°; R_F (ether) 0·38; and (iii) 1,3-dimethyluracil (3 mg, 5%), m.p. 118°; R_F (ether) 0·01.

Irradiation of 5,6-*Di-iodo*-1,3-*dimethyluracil* (11) *in Benzene*.—Irradiation of compound (11) (100 mg) in benzene (160 ml) for 90 min followed by work-up as before gave (i) 1,3-dimethyluracil (22) (2·3 mg, 6%), m.p. 118°; (ii) 1,3-dimethyl-5-phenyluracil (23) (12 mg, 20%), m.p. 144—145°; R_F (ether) 0·71; *m/e* 216 (M^+), 215 (M − H), 159 (M − CH_3NCO), 158 (159 − H), 131 (159 − CO), 130 (131 − H), 118 (159 − CH_3CN), and 117 (118 − H); δ ($CDCl_3$) 3·40 (3H, s, NMe), 3·45 (3H, s, NMe), 7·6 (1H, s, 6-H), and 7·4 (5H, m, aromatic); $\lambda_{max.}$ (EtOH) 285 (ε 7020) and 241 nm (5832); (iii) a trace of 5-iodo-1,3-dimethyluracil (18), R_F 0·70, mass spectrum identical with that of (18); (iv) 1,3-dimethyl-6-phenyluracil (28) (6 mg, 11%), m.p. 118—119°; R_F (ether) 0·75; (v) 6-biphenyl-2-yl-1,3-dimethyluracil (30), m.p. 160—164°; R_F (ether) 0·80; *m/e* 292 (M^+), 291 (M − H), 235 (M − CH_3NCO), 234 (235 − H), 206 (234 − CO), 205 (206 − H), 178 (205 − HCN), and 165 (206 − C_2HO); δ (CCl_4) 3·06 (3H, s, NMe), 3·86 (3H, s, NMe), 5·63 (1H, s, 5-H), and 7·1 (9H, m, aromatic); $\lambda_{max.}$ (EtOH) 280 nm (ε 9733); and (vi) 2,4-dimethyldibenzo-[*f*,*h*]quinazoline-1,3-dione [9,*] (31) (12 mg, 16%), m.p. 162—163° (lit.,[9] 162—163°); R_F (ether) 0·71; *m/e* 290 (M^+), 289 (M − H), 233 (M − CH_3NCO), 232 (289 − CH_3NCO), 205 (233 − CO), 204 (205 − H), 178 (205 − HCN), and 177 (204 − HCN); δ ($CDCl_3$) 3·52 (3H, s, NMe), 3·75 (3H, s, NMe), 9·78 (1H, dd), 8·40—8·73 (2H, m), 8·13 (1H, dd), and 7·46—7·94 (4H, m); $\lambda_{max.}$ (EtOH) 358 (ε 5437), 348 (5800), 333 (6162), 293 (8700), 263sh (22,837), and 252 nm (32,625).

Irradiation of 6-*Iodo*-1,3-*dimethyluracil* (16) *in Benzene*.—Irradiation of compound (16) (100 mg) in benzene (60 ml) for 2 h led to a mixture from which starting material (16 mg, 16%), 1,3-dimethyl-6-phenyluracil (28) (40 mg, 49%), and 1,3-dimethyluracil (22) (2 mg, 4%) were isolated.

Irradiation of 5-*Iodo*-1,3-*dimethyluracil* (18) *in Benzene*.—Irradiation of compound (18) (100 mg) in benzene (60 ml) for 2 h led to 1,3-dimethyl-5-phenyluracil (23) (44 mg, 54%) and traces of compounds (18) and (22).

Irradiation of 5-*Iodo*-1,3-*dimethyl*-6-*phenyluracil* (24) *in Benzene*.—Compound (24) (100 mg) in benzene (100 ml) was irradiated for 1 h with occasional shaking with sodium hydrogen sulphite solution. After work-up as before, three products were isolated and identified as the dibenzoquinazoline (31) (26 mg, 30%), 1,3-dimethyl-5,6-diphenyluracil (26) (7 mg, 8%) [m.p. 166—167°; *m/e* 292 (M^+); δ ($CDCl_3$) 3·14 (3H, s, NMe), 3·45 (3H, s, NMe), and 7·37 (10H, m, aromatic], and 6-biphenyl-2-yl-1,3-dimethyluracil (30) (trace).

Irradiation of 6-*Iodo*-1,3-*dimethyl*-5-*phenyluracil* (32) *in*

* There is a similarity between the n.m.r. spectra of (31) and phenanthrene.[13]

[12] G. Strauss, *Annalen*, 1960, **638**, 205.

[13] F. A. Bovey, 'Nuclear Magnetic Resonance Spectroscopy,' Academic Press, New York, 1969, p. 68.

Benzene.—Compound (32) (100 mg) in benzene (100 ml) was irradiated for 1 h with occasional shaking with sodium hydrogen sulphite solution. After work-up as before, the dibenzoquinazoline (31) (12 mg, 14%), and 1,3-dimethyl-5-phenyluracil (23) (2 mg, 2%) were obtained.

Irradiation of 6-Iodo-1,3-dimethyluracil (16) in the Presence of Biphenyl.—Irradiation of compound (16) (100 mg) and biphenyl (60 mg) in acetonitrile (100 ml) for 8 h led to three isolable products: the dibenzoquinazoline (31) (4 mg, 7%), 1,3-dimethyluracil (22) (12 mg, 25%), and starting material (16) (30 mg, 30%).

Irradiation of 6-Biphenyl-2-yl-1,3-dimethyluracil (30).—After irradiation of compound (30) (2 mg) in acetonitrile for 5 h, followed by work-up as usual, a trace of the dibenzoquinazoline (31) was observed.

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