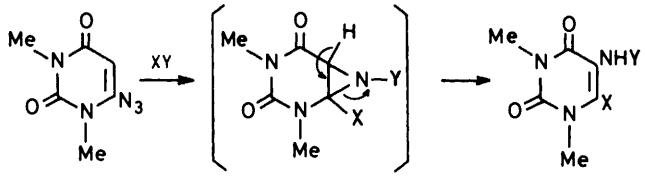
Pyrimidine Derivatives and Related Compounds. Part 50.[1] Photochemical Reaction of 5-Substituted 6-Azido-1,3-dimethyluracils with Nucleophiles. Ring Transformation of Pyrimidine to 1,3,5-Triazepine and Hydantoin Ring Systems[2]

Kosaku Hirota,* Kazuo Maruhashi, Norihiko Kitamura, Tetsuji Asao, and Shigeo Senda
Gifu Pharmaceutical University, 6-1 Mitahora-higashi 5 Chome, Gifu 502, Japan

Photolysis of 5-substituted 6-azidouracil derivatives in the presence of nucleophiles has been studied. Irradiation of 5-alkyl-6-azidouracils (**3**) in the presence of amines caused a ring expansion to give 1,3,5-triazepine derivatives (**7**). Photolysis of 6-azido-1,3,5-trimethyluracil (**3a**) in alcohols gave the corresponding 6,6-dialkoxy-5-amino-5,6-dihydrouracils (**8**). When compound (**3a**) was irradiated in water, a ring contraction occurred to afford 3,5-dimethylhydantoin (**9**). On the other hand, 6-azido-5-cyano-1,3-dimethyluracil (**4**) was converted into 1,3,5-triazepines (**13**) only in the presence of alcohols.

Several studies on the chemistry of azido compounds have been carried out because of their interesting reactivity and utility in organic synthesis as reagents or intermediates.[3] Aryl azides display a variety of thermochemical and photochemical reactivities.[4] For example, it has long been known that photolysis of phenyl azides in the presence of amines produces a ring expansion to give azepines.[5] Much effort has recently been expended in elucidating the reaction mechanism[6] of this conversion and in applying it to other aromatic azides.[7] On the other hand, although the isomerization between the azido group and the tetrazole ring for aromatic heterocyclic azides has been extensively investigated,[8] their ring expansion to seven-membered heterocycles has received less attention apart from a few examples.[6d,9]

We recently reported that the photolysis of 6-azido-1,3-dimethyluracil (**1**) with amines and acyl chlorides led to the formation of 6-alkylamino-5-amino-1,3-dimethyluracils (**2**; X = NRR', Y = H)[10] and 5-acylamino-6-chloro-1,3-dimethyluracils (**2**; X = Cl, Y = COR),[11] respectively, *via* an aziridine intermediate (**A**) (Scheme 1). In connection with these studies, it was clearly of interest to examine the photochemical reaction of 5-substituted 6-azidouracils with nucleophiles because of the predicted difficulty of converting the intermediate, corresponding to (**A**), into the 5-aminouracil (**2**).



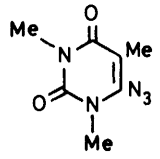
(1) (A) (2)

Scheme 1.

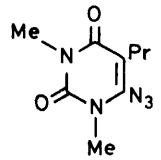
In this investigation 5-alkyl-6-azido-1,3-dimethyluracils (**3a** and **b**), 6-azido-5-cyano-1,3-dimethyluracil (**4**), and 6-azido-5-benzyl-3-methyluracil (**5**) were used as the 5-substituted derivatives. It was found that the photolysis of these compounds takes a quite different path from that of 5-unsubstituted uracils[10] and causes a ring transformation to give a 1,3,5-triazepine or hydantoin ring system.

Results and Discussion

5-Substituted 6-azidouracils (**3**)—(**5**), employed here as starting materials, were prepared by treating the corresponding 6-chlorouracils[12,13] with sodium azide.



(3a)



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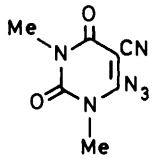
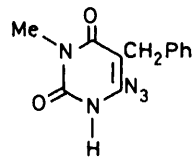


(4)



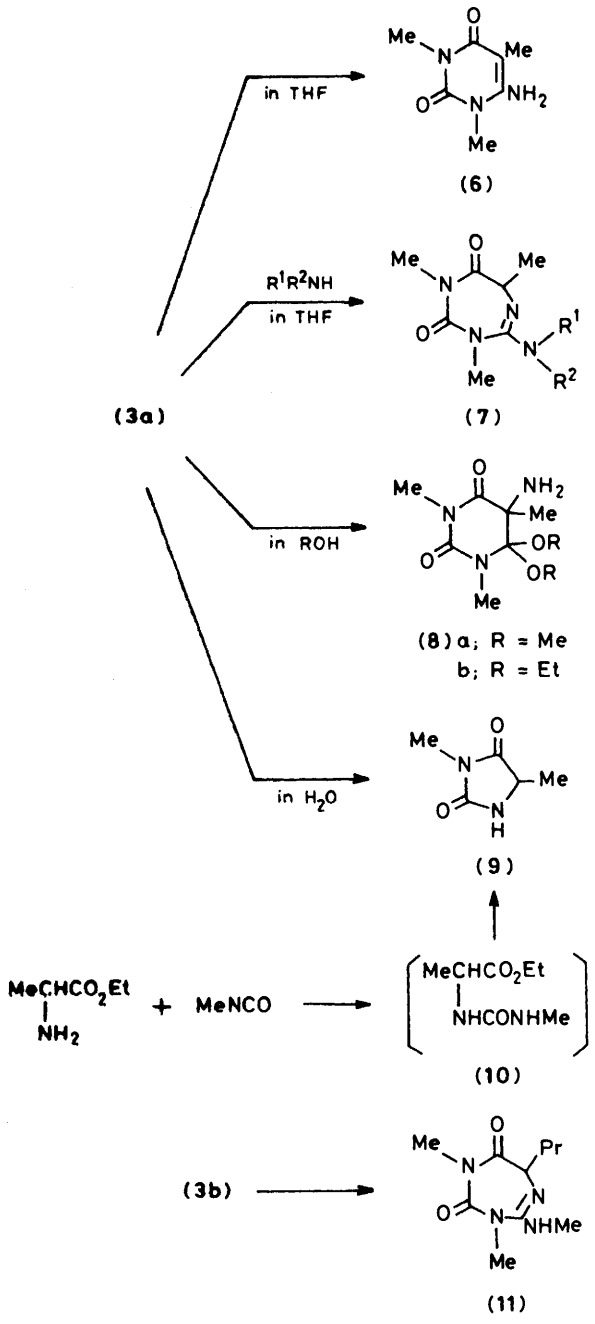
(5)

First, photolysis of 6-azido-1,3,5-trimethyluracil (**3a**) was carried out in the absence of any nucleophile. When a solution of (**3a**) in tetrahydrofuran (THF) was irradiated, a reduction product, 6-amino-1,3,5-trimethyluracil (**6**),[12] was formed.

On the other hand, irradiation of the azidouracil (**3a**) in the presence of methylamine in THF gave a ring-expansion product, 1,3,6-trimethyl-4-methylamino-2,3,6,7-tetrahydro-1*H*-1,3,5-triazepine-2,7-dione (**7a**), in 40% yield. The structure of (**7a**) was determined on the basis of elemental analysis and spectral data and is especially supported by the facts that the u.v. spectrum shows only end absorption, implying a non-resonant structure, and the signal of the methyl group at C-7 appears as a doublet at δ 1.43 in the ^{1}H n.m.r. spectrum. Similar treatment of the azidouracil (**3a**) with other primary or secondary alkylamines in THF afforded the corresponding 4-alkylamino-1*H*-1,3,5-triazepines (**7b**—**f**) as shown in the Table. Application of this ring transformation to 6-azido-1,3-dimethyl-5-propyluracil (**3b**) using methylamine as an amine afforded the 7-propyltriazepine (**11**) in 82% yield.

We also examined the photolysis of the azidouracil (**3a**) with alcohols in order to synthesize 4-alkoxy-1*H*-1,3,5-triazepines. A methanolic solution of compound (**3a**) was irradiated for 3 h. The product thus obtained was not the expected triazepine but 5-amino-6,6-dimethoxy-1,3,5-trimethyl-5,6-dihydrouracil (**8a**). Analogously, irradiation of the azide (**3a**) in ethanol gave the corresponding 6,6-diethoxy-5,6-dihydrouracil (**8b**).

Furthermore, irradiation of the azidouracil (**3a**) in water gave



Scheme 2.

an unexpected product, 3,5-dimethylhydantoin (**9**), in 58% yield. Its structure was determined by an alternative synthesis, namely treatment of alanine ethyl ester with methyl isocyanate followed by heating in hydrochloric acid to afford the hydantoin (**9**) without isolation of an open-chain urea (**10**) (Scheme 2).

Plausible mechanisms to explain the above results may be formulated as shown in Scheme 3. Photochemically initiated loss of nitrogen from the azide (**3a**) gives rise to a singlet nitrene (**B**); if there is no nucleophile nearby, the nitrene (**B**) undergoes intersystem crossing to give the triplet species (**C**) and its abstraction of hydrogen from the solvent yields the amine (**6**). Formation of the triazepines (**7**) involves nucleophilic addition of alkylamine to an azirine (**D**) which is in equilibrium with (**B**) and subsequent fission of the C-5–C-6 bond of the resulting aziridine (**E**). When alcohols are used as nucleophiles, the addition of another molecule of alcohol to an aziridine (**E**) at C-6 gives the 5,6-dihydrouracils (**8**). Bimolecular addition of water to the azirine (**D**) also gives a 5,6-dihydrouracil (**F**), which undergoes cleavage of the N-1–C-6 bond, re-intramolecular cyclization due to the amino group attacking the urea carbonyl group, and subsequent decarboxylation to give rise to the hydantoin (**9**).

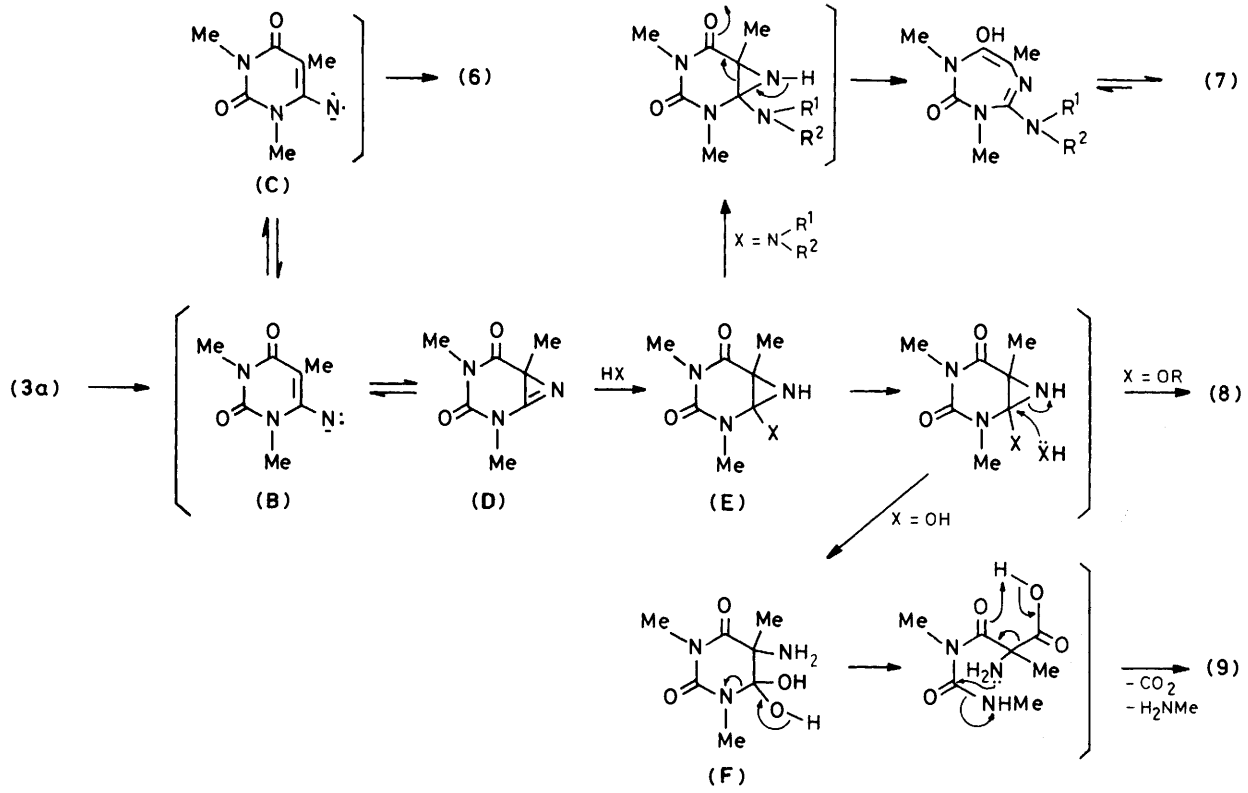
The photolysis of 6-azido-5-cyano-1,3-dimethyluracil (**4**), possessing an electron-withdrawing group as the 5-substituent, with alkylamines did not give the corresponding triazepine derivatives. When the cyano compound (**4**) was irradiated with diethylamine in THF, 5-cyano-6-diethylamino-1,3-dimethyluracil (**12**) was obtained. The identification of its structure was established by an alternative synthesis of this compound from 6-chloro-5-cyano-1,3-dimethyluracil. Compound (**12**) was also obtained by treatment of the azidouracil (**4**) with diethylamine without irradiation, indicating that formation of the uracil (**12**) does not need photochemical activation and that (**12**) is formed thermochemically by nucleophilic substitution. These unexpected results prompted us to examine the photolysis of the azidouracil (**4**) in the presence of much weaker nucleophiles such as alcohols or water. Although the irradiation of compound (**4**) in water did not give any isolatable product, in methanol 6-cyano-4-methoxy-1,3-dimethyl-2,3,6,7-tetrahydro-1*H*-1,3,5-triazepine-2,7-dione (**13a**) was formed in 75% yield. Other 4-alkoxy-1*H*-1,3,5-triazepines (**13b** and **c**) were obtained by similar photolysis of compound (**4**) in ethanol and propan-2-ol.

Similar treatment of 6-azido-5-benzyl-3-methyluracil (**5**) in the presence of dimethylamine gave the corresponding 6-benzyl-4-dimethylamino-1*H*-1,3,5-triazepine (**14**), although an intramolecular cyclization product, a pyrimido[4,5-*b*]quinoline derivative, is formed on irradiation of 6-azido-5-benzyl-1,3-dimethyluracil in the absence of amines.[14] These reactions are shown in Scheme 4.

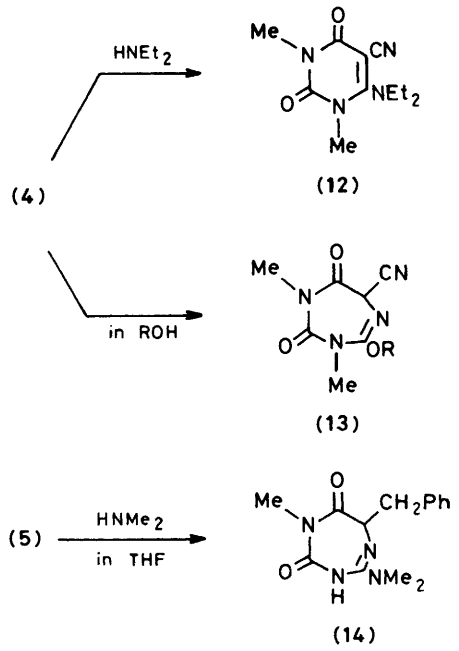
Table. Formation of 1*H*-1,3,5-triazepine-2,7-diones (**7**) and (**13**)

Compound	R^1R^2N (or OR)	Reaction time (h)	M.p. (°C)	Recrystallization solvent	Yield (%)
(7a)	MeNH	3	171—172.5	EtOH	40
(7b)	EtNH	3	151—152.5	EtOH	41
(7c)	Pr^iNH	6	150—152	EtOH	30
(7d)[a]	Me_2N	3	218—220	EtOH	57
(7e)[a]	Et_2N	8	202—205	MeOH	37
(7f)[a]	piperidino	3	187—189	EtOH	25
(13a)	MeO	3	169—170	MeOH	75
(13b)	EtO	3	109—110	Light petroleum	63
(13c)	Pr^iO	3	121—122	Light petroleum	53

[a] As the picrate salt.



Scheme 3.



Scheme 4.

Experimental

M.p.s were taken on a Yanagimoto melting point apparatus and are uncorrected. I.r. spectra were recorded with a Hitachi Model 215 spectrophotometer using KBr pellets. U.v. spectra were obtained from ethanol on a Hitachi 323 spectrophotometer. ^{1}H N.m.r. spectra were determined with a Hitachi Perkin-Elmer R-20B (60-MHz) instrument for solutions in $CDCl_3$ unless otherwise stated, using tetramethylsilane as internal standard. Chemical shifts are reported in p.p.m. (δ) and signals are quoted as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), or brs (broad singlet); *J* values are first order. ^{13}C N.m.r. spectra were recorded on a JEOL JNM-FX-100 Fourier transform spectrometer operating at 25.00 Mz, with tetramethylsilane as internal standard. Mass spectra were taken on a JEOL JMS-D300 machine operating at 70 eV. Irradiation was carried out at 25—30 °C in a flask equipped with a Pyrex-jacketted immersion lamp. The light source was a Riko-UVL 100 W high-pressure mercury lamp. Prior to irradiation, the solution was flushed with nitrogen and nitrogen was bubbled through the solution at a constant rate during irradiation.

6-*Azido*-1,3,5-*trimethyluracil* (**3a**).—A solution of 6-chloro-1,3,5-trimethyluracil[12] (5.0 g, 26.5 mmol) and sodium azide (2.1 g, 32.3 mmol) in dimethylformamide (DMF) (10 ml) was warmed at 70 °C for 3.5 h. The solvent was removed under reduced pressure and the residue was treated with water. The resulting precipitate was recrystallized from light petroleum (b.p. 50—90 °C) to give the 6-*azidouracil* (**3a**) (2.5 g, 48%), m.p. 101—103 °C; δ_H 2.19 (3 H, s, 5-Me), and 3.39 and 3.46 (each 3 H, s, NMe); $\nu_{max.}$ 2 140 cm^{-1} (N_3) (Found: C, 43.35; H, 4.7; N, 35.6. $C_7H_9N_5O_2$ requires C, 43.05; H, 4.65; N, 35.9%).

6-*Azido*-1,3-*dimethyl*-5-*propyluracil* (**3b**).—A solution of 6-chloro-1,3-dimethyl-5-propyluracil[12] (1.0 g, 5 mmol) and sodium azide (0.6 g, 10 mmol) in DMF (5 ml) was warmed at 70 °C for 6 h. The solvent was removed under reduced pressure and the residue was treated with water. The mixture was extracted with dichloromethane, and the extract was dried ($MgSO_4$) and evaporated to dryness. The resulting oily product, in which a small amount of 1,3-dimethyl-5-propylbarbituric acid was detected by n.m.r. spectroscopy and t.l.c., was used for the next step without purification. The n.m.r. spectrum of the

6-azidouracil (**3b**); δ_H 1.00 (3 H, t, *J* 6 Hz, CH_2CH_3), 1.23—1.80 (2 H, m, $CH_2CH_2CH_3$), 2.34 (2 H, t, *J* 7 Hz, 5-CH_2), and 3.32 and 3.36 (each 3 H, s, NMe).

6-*Azido*-5-*cyano*-1,3-*dimethyluracil* (**4**).—A solution of 6-chloro-5-cyano-1,3-dimethyluracil[13] (2.0 g, 10 mmol) and sodium azide (0.78 g, 12 mmol) in ethanol (20 ml) was stirred for 1 h at room temperature. The resulting precipitate was collected by filtration and recrystallized from methanol to give pale yellow needles (1.5 g, 73%), m.p. 180 °C. This compound is unstable and contains a small amount of deaza product, which is suggested to be 6-amino-5-cyano-1,3-dimethyluracil by t.l.c. and mass spectral analyses. Therefore, the recrystallized sample did not give satisfactory miroanalytical data for nitrogen. δ_H (CF_3CO_2H) 3.55 and 3.63 (each 3 H, s, NMe); $\nu_{max.}$ 2 160 (N_3) and 2 230 cm^{-1} (CN); *m/z* 206 (M^+) (Found: C, 40.8; H, 2.95; N, 39.8. $C_7H_6N_6O_2$ requires C, 40.8; H, 2.95; N, 40.75%).

6-*Azido*-5-*benzyl*-3-*methyluracil* (**5**).—To a solution of 5-benzyl-1-methylbarbituric acid (4.0 g, 17.2 mmol) and phosphoryl trichloride (18 ml) was added water (0.9 ml). The mixture was heated under reflux for 1.5 h. The reaction solution was evaporated to dryness and the residue was treated with water. The resulting precipitate was collected by filtration and recrystallized from ethyl acetate to give 5-*benzyl*-6-*chloro*-3-*methyluracil* (1.4 g, 30%), m.p. 190—191 °C; δ_H [$(CD_3)_2SO$] 3.18 (3 H, s, NMe), 3.72 (2 H, s, CH_2), 7.26 (5 H, s, Ph), and 12.25 (1 H, brs, exchangeable, NH) (Found: C, 57.45; H, 4.4; N, 11.1. $C_{12}H_{11}ClN_2O_2$ requires C, 57.5; H, 4.4; N, 11.2%).

A solution of the 6-chlorouracil (3.5 g, 14 mmol) and sodium azide (1.8 g, 28 mmol) in hexamethylphosphoramide (20 ml) was heated at 100 °C for 6 h. To the reaction mixture was added water (20 ml) and the solution was acidified with hydrochloric acid. The resulting precipitate was filtered, washed with water, and recrystallized from methanol to give the 6-*azido*-5-*benzyluracil* (**5**) (2.8 g, 79%), m.p. 232—234 °C; δ_H 3.30 (3 H, s, NMe), 3.70 (2 H, s, CH_2), and 7.24 (5 H, s, Ph); $\nu_{max.}$ 2 125 cm^{-1} (N_3) (Found: C, 55.8; H, 4.35; N, 27.05. $C_{12}H_{11}N_5O_2$ requires C, 56.0; H, 4.3; N, 27.25%).

6-*Amino*-1,3,5-*trimethyluracil* (**6**).—A solution of the 6-azidouracil (**3a**) (0.5 g, 2.6 mmol) in THF (250 ml) was irradiated for 5 h. After evaporation of the solvent, the residue was treated with diethyl ether to give the crude product. Recrystallization from ethyl acetate afforded pale yellow prisms (0.07 g, 16%), m.p. 252—253 °C (lit.,[12] 242—243 °C). This compound was identical with an authentic sample.[12] δ_H [$(CD_3)_2SO$] 1.75 (3 H, s, 5-Me), 3.11 and 3.27 (each 3 H, s, NMe), and 6.32 (2 H, brs, NH_2).

4-*Alkylamino*-1,3,6-*trimethyl*-2,3,6,7-*tetrahydro*-1H-1,3,5-*triazepine*-2,7-*diones* (**7a—f**).—A solution of the 6-azidouracil (**3a**) (0.5 g, 2.6 mmol) and an alkylamine (44 mmol), *i.e.* 40% aqueous methylamine, 70% aqueous ethylamine and isopropylamine, 50% aqueous dimethylamine, diethylamine, and piperidine, in THF (250 ml) was irradiated for 3 h. After evaporation of the solvent, the residue was treated with diethyl ether to give the corresponding 4-*alkylamino*-1,3,5-*triazepines* (**7a—c**). If the oily residue did not solidify, then it was dissolved in dry diethyl ether (5 ml) and a saturated ethereal solution of picric acid (5 ml) was added. The resulting precipitate was collected by filtration and recrystallized from an appropriate solvent to give the *picrates* of (**7d—f**) (see Table).

The 4-*methylaminotriazepine* (**7a**); δ_H 1.43 (3 H, d, *J* 6 Hz, 6-Me), 2.78 (3 H, d, *J* 4 Hz, NH*Me*), 3.10 and 3.23 (each 3 H, s, NMe), 3.93 (1 H, q, *J* 6 Hz, 6-H), and 4.05 (1 H, brs, exchangeable, NH); *m/z* 198 (M^+) (Found: C, 48.75; H, 7.25; N, 28.35. $C_8H_{14}N_4O_2$ requires C, 48.45; H, 7.1; N, 28.45%).

The 4-*ethylaminotriazepine* (**7b**); δ_H 1.15 (3 H, t, *J* 7.5 Hz, CH_2CH_3), 1.42 (3 H, d, *J* 6 Hz, 6-Me), 2.97—3.37 (2 H, m, CH_2CH_3), 3.11 and 3.25 (each 3 H, s, NMe), 3.85 (1 H, brs, exchangeable, NH), and 3.91 (1 H, q, *J* 6 Hz, 6-H) (Found: C, 50.8; H, 7.65; N, 26.6. $C_9H_{16}N_4O_2$ requires C, 50.95; H, 7.6; N, 26.4%).

The 4-*isopropylaminotriazepine* (**7c**); δ_H 1.15 (6 H, d, *J* 6 Hz, $CHMe_2$), 1.40 (3 H, d, *J* 6 Hz, 6-Me), 3.09 and 3.19 (each 3 H, s, NMe), 3.68 (1 H, brs, exchangeable, NH), 3.78 (1 H, septet, *J* 6 Hz, $CHMe_2$), and 3.89 (1 H, q, *J* 6 Hz, 6-H) (Found: C, 53.25; H, 8.1; N, 24.7. $C_{10}H_{18}N_4O_2$ requires C, 53.1; H, 8.0; N, 24.75%).

The 4-*dimethylaminotriazepine* (**7d**) *picrate*; δ_H 1.36 (3 H, d, *J* 7 Hz, 6-Me), 3.00 and 3.17 (each 3 H, s, NMe), 3.05 (6 H, s, NMe_2), 4.65 (1 H, q, *J* 7 Hz, 6-H), and 8.49 (2 H, s, aromatic H of picric acid) (Found: C, 41.05; H, 4.3; N, 22.3. $C_{15}H_{19}N_7O_9$ requires C, 40.8; H, 4.35; N, 22.2%).

The 4-*diethylaminotriazepine* (**7e**) *picrate*; δ_H 1.20 [6 H, t, *J* 7 Hz, $N(CH_2CH_3)_2$], 1.37 (3 H, d, *J* 7 Hz, 6-Me), 2.99 and 3.16 (each 3 H, s, NMe), 3.05—3.80 [4 H, m, $N(CH_2CH_3)_2$], 4.67 (1 H, q, *J* 7 Hz, 6-H), and 8.49 (2 H, s, aromatic H of picric acid) (Found: C, 43.55; H, 4.85; N, 20.9. $C_{17}H_{23}N_7O_9$ requires C, 43.4; H, 4.95; N, 20.9%).

The 4-*piperidinotriazepine* (**7f**) *picrate*; δ_H 1.38 (3 H, d, *J* 7 Hz, 6-Me), 1.50—1.80 and 3.25—3.56 (4 H and 2 H, m, piperidino-CH_2), 3.00 and 3.20 (each 3 H, s, NMe), 4.62 (1 H, q, *J* 7 Hz, 6-H), and 8.49 (2 H, s, aromatic H of picric acid) (Found: C, 45.2; H, 4.85; N, 20.15. $C_{18}H_{23}N_7O_9$ requires C, 44.9; H, 4.8; N, 20.35%).

5-*Amino*-6,6-*dimethoxy*-1,3,5-*trimethyl*-5,6-*dihydrouracil* (**8a**).—A solution of the 6-azidouracil (**3a**) (0.5 g, 2.6 mmol) in methanol (250 ml) was irradiated for 3 h. After removal of the solvent, the residue was treated with light petroleum (b.p. 30—60 °C), the resulting crystals were collected by filtration, and recrystallized from light petroleum (b.p. 50—90 °C) to give the 5,6-*dihydrouracil* (**8a**) (0.25 g, 43%), m.p. 91—95 °C; δ_H 1.20 (3 H, s, 5-Me), 1.82 (2 H, brs, exchangeable, NH_2), 3.15 and 3.65 (each 3 H, s, NMe), and 3.18 (6 H, s, 2 × OMe); *m/z* 231 (M^+) (Found: C, 46.95; H, 7.3; N, 18.4. $C_9H_{17}N_3O_4$ requires C, 46.75; H, 7.4; N, 18.15%).

5-*Amino*-6,6-*diethoxy*-1,3,5-*trimethyl*-5,6-*dihydrouracil* (**8b**) *Picrate*.—A solution of the 6-azidouracil (**3a**) (0.5 g, 2.6 mmol) in ethanol (250 ml) was irradiated for 5 h. After removal of the solvent under reduced pressure, the residue was dissolved in dry diethyl ether (5 ml) and a saturated ethereal solution of picric acid (5 ml) was added. The resulting precipitate was recrystallized from ethanol to give the *picrate* of (**8b**) (0.06 g, 5%), m.p. 129—132 °C; δ_H 1.17 and 1.28 (each 3 H, t, *J* 7 Hz, OCH_2CH_3), 1.52 (3 H, s, 5-Me), 3.13 and 3.18 (each 3 H, s, NMe), 3.73 and 3.85 (each 2 H, q, *J* 7 Hz, OCH_2CH_3), 7.40 (2 H, br, NH_2), and 8.63 (2 H, s, aromatic H of picric acid) (Found: C, 41.9; H, 4.95; N, 17.4. $C_{17}H_{24}N_6O_{11}$ requires C, 41.8; H, 4.95; N, 17.2%).

3,5-*Dimethylhydantoin* (**9**).—(*a*) A solution of the 6-azidouracil (**3a**) (0.5 g, 2.6 mmol) in water (250 ml) was irradiated for 3 h. After removal of the solvent under reduced pressure, the residue was treated with diethyl ether. The separated crystals were recrystallized from ethanol to give the *hydantoin* (**9**) (0.19 g, 58%), m.p. 110—111 °C; δ_H 1.45 (3 H, d, *J* 7 Hz, 5-Me), 3.02 (3 H, s, NMe), 4.10 (1 H, q, *J* 7 Hz, 5-H), and 6.80 (1 H, brs, exchangeable, NH); *m/z* 128 (M^+) (Found: C, 47.1; H, 6.3; N, 21.9. $C_5H_8N_2O_2$ requires C, 46.85; H, 6.3; N, 21.85%).

(*b*) Triethylamine (0.8 g, 7.9 mmol) was added to a suspension of ethyl alaninate hydrochloride (1.0 g, 6.5 mmol) in THF (20 ml). The mixture was stirred for 1 h and the resulting precipitate was removed by filtration. The filtrate was evaporated under

reduced pressure and methyl isocyanate (5 ml) was added to the residue. The precipitating urea (**10**) was separated by decantation after being washed with diethyl ether. A solution of the urea (**10**) in 25% hydrochloric acid (5 ml) was heated at 100 °C for 1 h. After the solution had cooled, the separated crystals were collected by filtration and recrystallized from ethanol to give the hydantoin (**9**) (0.32 g, 38%), identical with the product obtained above.

1,3-*Dimethyl*-4-*methylamino*-6-*propyl*-2,3,6,7-*tetrahydro*-1H-1,3,5-*triazepine*-2,7-*dione* (**11**).—A solution of the 6-azido-5-propyluracil (**3b**) (0.5 g, 2.3 mmol) and 30% aqueous methylamine (3.0 g, 38 mmol) in THF (250 ml) was irradiated for 2 h. After removal of the solvent by evaporation, the residue was treated with diethyl ether and the resulting precipitate was collected by filtration. Recrystallization from ethyl acetate afforded the *triazepine* (**11**) (0.42 g, 82%), m.p. 155—157 °C; δ_H 0.94 (3 H, t, *J* 6 Hz, CH_2CH_3), 1.10—2.08 (4 H, m, $CH_2CH_2CH_3$), 2.83 (3 H, s, NH*Me*), 3.12 and 3.26 (each 3 H, s, NMe), 3.74 (1 H, dd, *J* 6 and 7 Hz, 6-H), and 4.13 (1 H, brs, exchangeable, NH) (Found: C, 52.85; H, 7.8; N, 24.5 $C_{10}H_{18}N_4O_2$ requires C, 53.1; H, 8.0; N, 24.75%).

5-*Cyano*-6-*diethylamino*-1,3-*dimethyluracil* (**12**).—(*a*) To a solution of the 6-azido-5-cyanouracil (**4**) (0.5 g, 2.4 mmol) in THF (20 ml) was added diethylamine (0.18 g, 2.4 mmol). The mixture was stirred for 5 min at room temperature and then evaporated to dryness. The residue was recrystallized from ethanol to give pale yellow needles of the 6-*diethylaminouracil* (**12**) (0.43 g, 75%), m.p. 117—118 °C; $\nu_{max.}$ 2 200 cm^{-1} (CN); δ_H 1.25 [6 H, t, *J* 7 Hz, $N(CH_2CH_3)_2$], 3.40 and 3.43 (each 3 H, s, NMe), and 3.47 [4 H, q, *J* 7 Hz, $N(CH_2CH_3)_2$] (Found: C, 56.05; H, 6.75; N, 23.85. $C_{11}H_{16}N_4O_2$ requires C, 55.9; H, 6.8; N, 23.7%).

(*b*) A mixture of 6-chloro-5-cyano-1,3-dimethyluracil [13] (0.5 g, 2.5 mmol) and diethylamine (2 ml) in methanol (20 ml) was stirred for 30 min at room temperature and then evaporated to dryness. Water (20 ml) was added to the residue and the separated product was recrystallized from ethanol to give the 6-diethylaminouracil (**12**) (0.49 g, 85%), identical with the product obtained above.

4-*Alkoxy*-6-*cyano*-1,3-*dimethyl*-2,3,6,7-*tetrahydro*-1H-1,3,5-*triazepine*-2,7-*diones* (**13**).—A solution of the 5-cyano-6-azidouracil (**4**) (0.5 g, 2.4 mmol) in an alcohol (250 ml), *i.e.* methanol, ethanol, or propan-2-ol, was irradiated for 3 h. After removal of the solvent by evaporation, the residue was recrystallized from an appropriate solvent to give the *triazepines* (**13**) (see Table).

The 4-*methoxytriazepine* (**13a**); $\delta_H[(CD_3)_2SO]$ 3.07 and 3.11 (each 3 H, s, NMe), 3.82 (3 H, s, OMe), and 5.83 (1 H, s, 6-H); $\nu_{max.}$ 2 260 cm^{-1} (CN) (Found: C, 46.0; H, 4.7; N, 26.85. $C_8H_{10}N_4O_3$ requires C, 45.7; H, 4.8; N, 26.6%).

The 4-*ethoxytriazepine* (**13b**); δ_H 1.37 (3 H, t, *J* 7 Hz, CH_2CH_3), 3.26 (6 H, s, 2 × NMe), 4.33 (2 H, q, *J* 7 Hz, CH_2CH_3), and 5.17 (1 H, s, 6-H); $\nu_{max.}$ 2 260 cm^{-1} (CN) (Found: C, 48.35; H, 4.9; N, 24.85. $C_9H_{12}N_4O_3$ requires C, 48.2; H, 5.35; N, 25.0%).

The 4-*isopropoxytriazepine* (**13c**); δ_H 1.35 (6 H, d, *J* 6 Hz, $CHMe_2$), 3.22 and 3.25 (each 3 H, s, NMe), 5.12 (1 H, septet, *J* 6 Hz, CH), and 5.14 (1 H, s, 6-H); $\nu_{max.}$ 2 260 cm^{-1} (CN) (Found: C, 50.3; H, 5.9; N, 23.5. $C_{10}H_{14}N_4O_3$ requires C, 50.4; H, 5.95; N, 23.5%).

6-*Benzyl*-4-*dimethylamino*-1-*methyl*-2,3,6,7-*tetrahydro*-1H-1,3,5-*triazepine*-2,7-*dione* (**14**).—A solution of the 6-azido-5-benzyluracil (**5**) (0.5 g, 1.9 mmol) and 40% aqueous dimethylamine (2.6 g, 23 mmol) in THF (250 ml) was irradiated for 1 h. After removal of the solvent by evaporation, the residue was treated with ethyl acetate and the resulting precipitate was collected by filtration and recrystallized from ethanol to give the *triazepine* (**14**) as prisms (0.4 g, 79%), m.p. 192—195 °C; $\delta_H[(CD_3)_2SO]$ 2.96 (6 H, s, NMe_2), 3.07 (3 H, s, NMe), 3.17 (1 H, d, *J* 6 Hz, 6-CH_AH), 4.00 (1 H, dd, *J* 6 and 8 Hz, 6-H), 7.27 (5 H, s, Ph), and the signal for 6-CH_BH (1 H, d, *J* 8 Hz) at 3.12 overlaps with that of NMe (δ 3.07); $\delta_C[(CD_3)_2SO]$ 31.4 (q, NMe_2), 32.8 (t, CH_2), 37.7 (q, NMe), 56.4 (d, CH), 126.6, 128.4, and 129.2 (each d, 5 C of Ph), 137.4 (s, 1 C of Ph), 155.4 and 156.6 (each s, together CO and C=N), and 170.6 p.p.m. (s, CO); *m/z* 274 (M^+) (Found: C, 61.15; H, 6.6; N, 20.25. $C_{14}H_{18}N_4O_2$ requires C, 61.3; H, 6.6; N, 20.45%).

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