Derivatives of Acetoacetic Acid. Part VI. A Synthesis of 1 : 3-Oxazine Derivatives employing Diketen.†*

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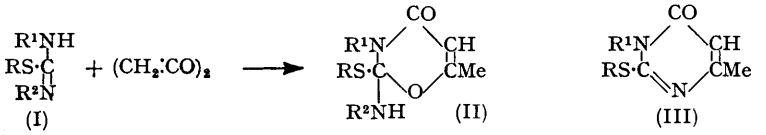
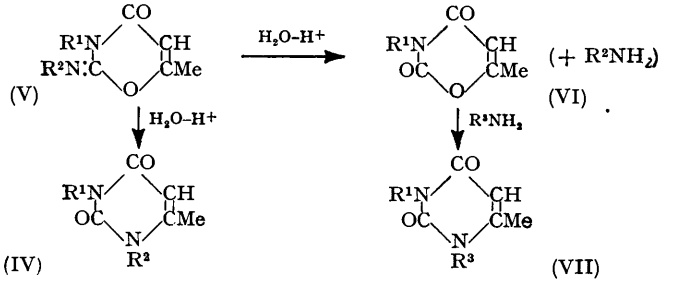
Diketen reacts with *NN'*-disubstituted derivatives of *S*-alkylthiourea to give 2-imino-1 : 3-oxazine derivatives with the elimination of thiol. The reaction is general, and the substituents may be alkyl, aryl, or aralkyl. Acid hydrolysis of the products gives dihydro-2 : 4-dioxo-1 : 3-oxazines, with elimination of amine, and, in certain cases, uracils, arising from the rearrangement of the imino-oxazine. The dihydro-dioxo-1 : 3-oxazines react with ammonia and with alkyl- and aralkyl-amines to give substituted uracils, affording a new route of wide applicability to these compounds.

In Part V *, it was shown that reaction of diketen with *S*-alkylthioureas (I; R^1 = H, Ph, or Me, R^2 = H) does not directly afford the pyrimidones expected by analogy with the well-known reaction of *S*-alkylthioureas and acetoacetic esters, but gives dihydro-1 : 3-oxazines (II), from which the pyrimidones (III) are obtained by treatment with basic catalysts. It was expected that *NN'*-disubstituted *S*-alkylthioureas with diketen might afford 1 : 3-oxazines (an almost unknown ring system), although they would not be convertible into 2-(alkylthio)pyrimidones.



However, the reaction of *NN'*-diethyl-*S*-methylthiourea with diketen in boiling benzene was accompanied by the elimination of methanethiol. Analysis showed the product, m. p. 30°, to be isomeric with 1 : 3-diethyl-6-methyluracil (IV; $R^1 = R^2$ = Et) but it was obviously distinct from this (Behrend and Hoffmann, *Annalen*, 1889, **253**, 71, give m. p. 52—53° for the uracil) and has been identified as (V; $R^1 = R^2$ = Et). Treatment of the



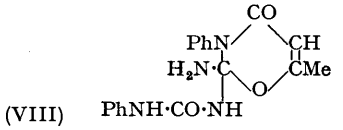
product with hot dilute acid gave ethylamine and (VI; R^1 = Et). Confirmation of these assignments was afforded by the reaction of the dihydro-2 : 4-dioxo-1 : 3-oxazine (VI; R^1 = Et) with amines—ammonia and ethylamine readily afforded the known 3-ethyl-6-methyluracil (VII; R^1 = Et, R^3 = H) and 1 : 3-diethyl-6-methyluracil (VII; $R^1 = R^3$ = Et), respectively—and by light-absorption evidence (see Table). The formation of uracils from dihydrodioxo-1 : 3-oxazines and amines affords a new and useful route to these compounds.

S-Methyl-, *S*-ethyl-, and *S*-benzyl-*NN'*-diphenylthiourea all reacted similarly with diketen (the last in toluene), giving the expected 1 : 3-oxazines. Acid hydrolysis of (V; $R^1 = R^2$ = Ph) gave a mixture from which only the expected dihydrodioxo-1 : 3-oxazine (VI; R^1 = Ph) was isolated. This compound with methylamine gave, 1 : 6-dimethyl-3-phenyluracil (VII; R^1 = Ph, R^3 = Me), but the reaction with ammonia was

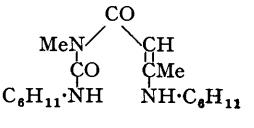
* Part V, preceding paper.

† Patents pending: B.P. Appln. 14535/52, 14644/52.

anomalous giving a product, $C_{18}H_{18}O_3N_4$, acid hydrolysis of which gave 6-methyl-3-phenyluracil, ammonia, and aniline; and, on the basis of this and light-absorption evidence (see Table), the product is regarded as (VIII), arising from two mols. of dihydrodioxo-1 : 3-oxazine and one of ammonia, with the elimination of acetoacetic acid.



(VIII)



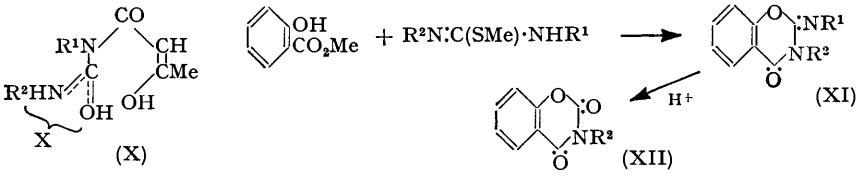
(IX)

It was not possible to replace diketen by an acetoacetic ester, which failed to react in the above preparations. Diketen was without effect on ethyl *N*-phenylurethane, which might have been expected to give the dihydrodioxo-1 : 3-oxazine (VI; R^1 = Ph) by elimination of ethanol.

NS-Dimethyl-*N'*-phenylthiourea with diketen gave high yields of an oxazine (V; R^1 = Me, R^2 = Ph), the structure of which was established by acid hydrolysis to the dihydro-3-methyl-2 : 4-dioxo-1 : 3-oxazine (VI; R^1 = Me) and aniline. A second substance from the above hydrolysis, isomeric with the starting material, is believed to be 3 : 6-dimethyl-1-phenyluracil (IV; R^1 = Me, R^2 = Ph) which, in common with other 1-aryluracils, is not available by the usual routes. The proportions of dihydrodioxo-1 : 3-oxazine and uracil obtained were dependent on the acid concentration, lower concentrations favouring dihydrodioxo-1 : 3-oxazine formation. (VI; R^1 = Me) reacted with ammonia, methylamine, and benzylamine, giving the expected uracils (VII; R^1 = Me, R^3 = H, Me, or CH_2Ph, respectively), but with *cyclo*hexylamine two mols. of amine reacted to give a substituted β-aminocrotonamide (IX). None of the dihydrodioxo-1 : 3-oxazines condensed with aromatic amines, either alone or in the presence of catalysts.

N-Benzyl-*S*-methyl-*N'*-phenylthiourea with diketen in boiling ethylene dichloride gave a 77% yield of the oxazine (V; R^1 = CH_2Ph, R^2 = Ph); structural proof was afforded by acid hydrolysis to (VI; R^1 = CH_2Ph) and aniline, although the main product was 3-benzyl-6-methyl-1-phenyluracil (IV; R^1 = CH_2Ph, R^2 = Ph). Higher acid concentrations favoured formation of dihydrodioxo-1 : 3-oxazine, which gave the expected uracils (VII; R^1 = CH_2Ph, R^3 = H) and (VII; R^1 = CH_2Ph, R^3 = Me) with ammonia and methylamine, respectively, providing further confirmation of the structures.

Hydrolysis of the imino-oxazines (V) with aqueous alkali gave the corresponding *NN'*-disubstituted ureas, although (V; R^1 = Me, R^2 = Ph) gave also 3 : 6-dimethyl-1-phenyluracil.

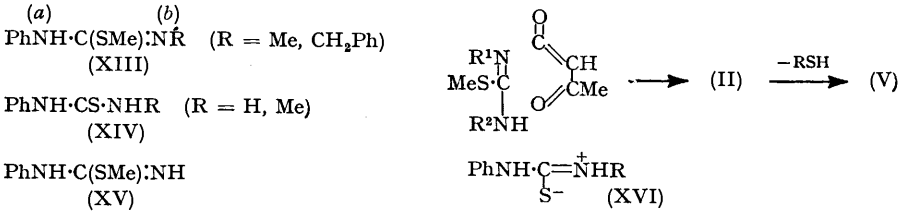


(X) (XI) (XII)

Formation of both a dihydrodioxo-1 : 3-oxazine and a uracil by the acid hydrolysis of certain of the imino-oxazines can be ascribed to the reactions of a common intermediate (X) which, by elimination of $R^2NH_3^+$ gives the dihydrodioxo-oxazine and by removal of H_3O^+ the uracil. It is unlikely that reaction of dihydrodioxo-1 : 3-oxazines (VI) with amines proceeds through the imino-oxazines (V), since the latter do not rearrange to uracils under the weakly alkaline conditions employed. The mechanism is probably similar to that generally assigned to the formation of amides from esters with amines.

Attention is drawn to the reaction of *S*-alkylthioureas with methyl or phenyl salicylate to give benzoxazine derivatives (XI; R^1 = R^2 = Ph; R^1 = R^2 = *o*-Me·C_6H_4; R^1 = R^2 = *p*-Me·C_6H_4; R^1 = Ph, R^2 = *p*-Br·C_6H_4; R^1 = Ph, R^2 = H) (Deck and Dains, *J. Amer. Chem. Soc.*, 1933, **55**, 4986), which, on hydrolysis with acids, gave dihydrodioxobenzoxazines (XII). In the two cases in which unsymmetrical *S*-substituted thioureas were employed, the phenylimino-derivatives were obtained.

Diketen reacted with the two unsymmetrical *S*-alkylthioureas (XIII) studied to give high yields of a single product in each case. It is also significant that the acetoacetyl radical in both cases became attached to the nitrogen atom (*b*) bearing the alkyl or aralkyl substituent, giving phenylimino-derivatives. This is in contrast to the reaction with *N*-methyl-*N'*-phenylthiourea, *N*-phenylthiourea (XIV), and *S*-methylphenylthiourea (XV)



(see Part V) where, in all three cases, the acetoacetyl radical became attached to the nitrogen atom (*a*) bearing the phenyl group. It might be expected that in all cases the reagent would attack nitrogen atom (*b*) in preference to that substituted by phenyl, and, in consequence, the less basic. However, other apparent anomalies have been reported. *S*-Methylphenylthiourea on treatment with methyl iodide gives *NS*-dimethyl-*N*-phenylthiuronium iodide [*i.e.*, substitution at (*a*)](Bertram, *Ber.*, 1892, **25**, 52), whereas treatment with phenyl *iso*cyanate, which in many reactions resembles diketen in reactivity (cf. Petersen, *Ber.*, 1950, **83**, 551), gives a substituted urea arising from attack at (*b*) (Lakra and Dains, *J. Amer. Chem. Soc.*, 1929, **51**, 2224).

The reaction of diketen with substituted thioureas can possibly be explained in terms of the dipolar " zwitterion " (XVI) that has been postulated to represent most closely the structure of thioureas (cf. Taylor and Baker, " Sidwick's Organic Chemistry of Nitrogen," Oxford, 1937, p. 281), in which the more basic nitrogen atom is closely bound with the sulphur atom, leaving the less basic nitrogen atom free to react. Nevertheless, certain facts await a satisfactory explanation. It was established that the reaction of diketen with substituted *S*-alkylthioureas is not of the Diels–Alder type (as written above, the disputed acetylketen structure being assigned to diketen), since *NN*-diethyl-*S*-methyl-*N'*-phenylthiourea failed to react with diketen, showing that a replaceable hydrogen is necessary.

Light-absorption data for certain of the imino-oxazines and dioxo-1 : 3-oxazines are tabulated below. The oxazines show the absorption expected for derivatives of crotonic acid, and the values of $\lambda_{max.}$ show that the presence of the phenylimino-group causes a considerable auxochromic shift of the absorption maximum, indicating some degree of interaction between the imino-group and the conjugated system.

Light-absorption data (in ethanol solution).

	$\lambda_{max.}$, Å	$\varepsilon_{max.}$		$\lambda_{max.}$, Å	$\varepsilon_{max.}$
(V; $R^1 = R^2 =$ Et)	2150 [1]	10,000	(VI; $R^1 =$ Et)	2300	7,200
	2560	1,950			
(V; $R^1 = R^2 =$ Ph)	2300	14,000	(VI; $R^1 =$ Ph)	2340	9,550
	2500 [2]	11,000			
(V; $R^1 =$ Me, $R^2 =$ Ph) ...	2500	11,500	(VIII)	2390	22,000
				2620	10,000

[1] End absorption. [2] Inflection.

Experimental

M. p.s were determined on a Kofler block and are corrected.

3-Ethyl-2-ethylimino-2 : 3-dihydro-6-methyl-4-oxo-1 : 3-oxazine (V; $R^1 = R^2 =$ Et).—*NN'*-Diethylthiourea (39·6 g.), methyl iodide (50 g.), and ethanol (200 c.c.) were refluxed for 1 hr., and most of alcohol then distilled off. The residue was treated with sodium hydroxide solution (10%; 120 c.c.) and, after being saturated with salt, the mixture was thoroughly extracted with ether to give, after drying and evaporation of the extracts, crude *NN'*-diethyl-*S*-methylthiourea (44 g.) as a pale yellow oil. This was treated in boiling benzene (50 c.c.) with diketen

(26 g.), added during 0·5 hr. with agitation; methanethiol was freely evolved. After a further 0·5 hr.'s refluxing the benzene was evaporated and the residue distilled, giving the *oxazine* (V; $R^1 = R^2 = Et$) (42·1 g., 77% yield on *NN'*-diethylthiourea), b. p. 90—93°/1 mm., m. p. 30° (Found: C, 59·7; H, 8·0; N, 15·1. $C_9H_{14}O_2N_2$ requires C, 59·3; H, 7·75; N, 15·4%). Light absorption: see Table.

3-*Ethyl*-2 : 3-*dihydro*-6-*methyl*-2 : 4-*dioxo*-1 : 3-*oxazine* (VI; $R^1 = Et$).—The oxazine (V; $R^1 = R^2 = Et$) (2·3 g.) was refluxed with a mixture of concentrated hydrochloric acid (1 c.c.) and water (10 c.c.) for 15 min., and then cooled. The separated *oxazine* (VI; $R^1 = Et$) (1·1 g.) was crystallised from light petroleum (b. p. 60—80°), giving needles, m. p. 69—70° (Found: C, 53·85; H, 5·55; N, 9·2. $C_7H_9O_3N$ requires C, 54·2; H, 5·85; N, 9·05%). Addition of alkali to the aqueous filtrate afforded ethylamine. Use of sulphuric acid in the above hydrolysis gave similar results. Light absorption: see Table.

Treatment of the 2 : 4-dioxo-1 : 3-oxazine (VI; $R^1 = Et$) (0·1 g.) with ammonia solution (*d* 0·88; 10 c.c.) gave, on evaporation, 3-ethyl-6-methyluracil, m. p. and mixed m. p. 206° (Hoebel, *Annalen*, 1907, **353**, 245, gives m. p. 195°). Similarly, treatment with 40% ethylamine gave 1 : 3-diethyl-6-methyluracil, as an oil which crystallised from ether as plates, m. p. 50—51° (Behrend and Hoffmann, *loc. cit.*, give m. p. 52—53°).

2 : 3-*Dihydro*-6-*methyl*-4-*oxo*-3-*phenyl*-2-*phenylimino*-1 : 3-*oxazine* (V; $R^1 = R^2 = Ph$).—*S*-Methyl-*NN'*-diphenylthiourea (24·2 g.) in boiling benzene (100 c.c.) was treated with diketen (8·4 g.), added with agitation during 0·5 hr. The product was refluxed for 5 hr., methanethiol being evolved, filtered and cooled, giving the *oxazine* (V; $R^1 = R^2 = Ph$) (18·9 g., 65%), which formed prisms, m. p. 184—185°, from ethyl acetate (Found: C, 73·0; H, 4·8; N, 10·2. $C_{17}H_{14}O_2N_2$ requires C, 73·35; H, 5·05; N, 10·0%). Light absorption: see Table.

S-Ethyl-*NN'*-diphenylthiourea similarly gave the corresponding oxazine in 36·5% yield. Crude *S*-benzyl-*NN'*-diphenylthiourea (cf. Werner, *J.*, 1890, 297), prepared from *NN'*-diphenylthiourea (46·0 g.) and benzyl chloride (25 g.), in toluene (100 c.c.), was treated with diketen (17·3 g.) as described above. Evaporation of the solvent left a gummy solid, which, when rubbed with benzene, gave the oxazine (20·0 g., 36%), m. p. 178—180°.

2 : 3-*Dihydro*-6-*methyl*-2 : 4-*dioxo*-3-*phenyl*-1 : 3-*oxazine* (VI; $R^1 = Ph$).—The oxazine (V; $R^1 = R^2 = Ph$) (2·0 g.) was refluxed with concentrated hydrochloric acid (1 c.c.) and water (10 c.c.) for 20 min. and then cooled. After two crystallisation of the precipitate from methanol the *oxazine* (VI; $R^1 = Ph$) was obtained as needles (0·7 g.), m. p. 170° (Found: C, 65·3; H, 4·45; N, 7·0. $C_{11}H_9O_3N$ requires C, 65·0; H, 4·45; N, 6·9%). Light absorption: see Table.

The 2 : 4-dioxo-1 : 3-oxazine (VI; $R^1 = Ph$) (0·1 g.) was warmed with aqueous methylamine (40%; 10 c.c.), and the solution then concentrated; 1 : 6-dimethyl-3-phenyluracil, m. p. and mixed m. p. 210°, was obtained (cf. Part V). Similar treatment with ammonia readily gave needles [probably (VIII)], m. p. 201°, from water (Found: C, 64·15; H, 5·4; N, 16·7. $C_{18}H_{18}O_3N_4$ requires C, 63·9; H, 5·35; N, 16·55%). Hydrolysis of (VIII) with boiling dilute hydrochloric acid gave 6-methyl-3-phenyluracil, m. p. and mixed m. p. 255—256° (Behrend, Meyer, and Buchholz, *Annalen*, 1901, **314**, 209, give m. p. 244—245°), and, on addition of alkali to the filtrate, ammonia and aniline. Light absorption of (VIII): see Table.

2 : 3-*Dihydro*-3 : 6-*dimethyl*-4-*oxo*-2-*phenylimino*-1 : 3-*oxazine* (V; $R^1 = Me$, $R^2 = Ph$).—*NS*-Dimethyl-*N'*-phenylthiourea (Deck and Dains, *loc. cit.*) (34·5 g.) in boiling benzene (50 c.c.) was treated with diketen (16·5 g.) during 0·5 hr., and refluxing continued for 3 hr., methanethiol being evolved. The solvent was evaporated and the oil (42 g.) rubbed with ether–light petroleum (b. p. 40—60°) giving the *oxazine* (V; $R^1 = Me$, $R^2 = Ph$) as a pale brown solid (30·5 g., 95%) which, on crystallisation from aqueous methanol, gave prisms, m. p. 69—70° (Found: C, 66·95; H, 5·35; N, 12·6. $C_{12}H_{12}O_2N_2$ requires C, 66·65; H, 5·6; N, 12·95%). Light absorption: see Table.

2 : 3-*Dihydro*-3 : 6-*dimethyl*-2 : 4-*dioxo*-1 : 3-*oxazine* (VI; $R^1 = Me$).—The oxazine (V; $R^1 = Me$, $R^2 = Ph$) (1·0 g.) was refluxed with concentrated hydrochloric acid (1 c.c.) and water (10 c.c.) for 20 min. On cooling, a microcrystalline powder (0·05 g.), m. p. 300—302°, was first deposited, followed by the *oxazine* (VI; $R^1 = Me$) (0·4 g.) as needles (from water), m. p. 108—109° (Found: C, 51·35; H, 4·8; N, 9·95. $C_6H_7O_3N$ requires C, 51·05; H, 5·0; N, 9·95%). Recrystallisation of the high-melting product first deposited gave 3 : 6-*dimethyl*-1-*phenyluracil* (IV; $R^1 = Me$, $R^2 = Ph$) as plates, m. p. 300—302°, from water (Found: C, 66·35; H, 5·65; N, 12·7. $C_{12}H_{12}O_2N_2$ requires C, 66·65; H, 5·6; N, 12·95%).

Further hydrolyses of the phenylimino-oxazine (V; $R^1 = Me$, $R^2 = Ph$) (10·0 g.) with the calculated amount of concentrated hydrochloric acid (4·2 c.c.) were carried out with varying amounts of water and 0·5 hr.' boiling. The solid products were isolated by means of chloroform,

and the dioxo-1 : 3-oxazine separated from the uracil by Soxhlet extraction with methanol, in which the uracil is practically insoluble. The results are presented below:

Water (c.c.)	10	20	40
Dioxo-1 : 3-oxazine (g.)	5·10	5·51	5·63
Uracil (g.)	0·80	0·49	0·28

The dioxo-1 : 3-oxazine (VI; R^1 = Me) (0·2 g.) was warmed with ammonia solution (*d* 0·88; 10 c.c.) and the solution evaporated to a small bulk, giving 3 : 6-dimethyluracil, m. p. and mixed m. p. 274° (Behrend and Hesse, *Annalen*, 1903, **329**, 348, give m. p. 261—262°). Similarly, treatment with aqueous methylamine (40%) gave 1 : 3 : 6-trimethyluracil as needles, m. p. and mixed m. p. 110° (Behrend and Hufschmidt, *Annalen*, 1905, **343**, 158, give m. p. 111—112°). The dioxo-1 : 3-oxazine (1·4 g.) and benzylamine (1·2 g.) were refluxed in ethanol (10 c.c.) for 2 hr., followed by removal of the solvent under reduced pressure and extraction of the residue with ether. Removal of the ether, trituration of the resulting oil with water and crystallisation of the solid from ether gave plates (0·85 g.), m. p. 84—85° undepressed with an authentic specimen of 1-benzyl-3 : 6-dimethyluracil (Wheeler and McFarland, *Amer. Chem. J.*, 1909, **42**, 105, give m. p. 85—86°).

When the dioxo-1 : 3-oxazine (0·1 g.) was heated with *cyclo*hexylamine (0·1 g.) at 90—100° for 1 hr. and the oil rubbed with ether, a solid (0·06 g.), m. p. 135—138°, was obtained. Crystallisation from aqueous methanol gave N-cyclo*hexyl*-N′-(β-cyclo*hexylaminocrotonyl*)-N′-*methylurea* (IX) as needles, m. p. 139—140° (Found: C, 67·55; H, 10·05; N, 12·9. $C_{18}H_{31}O_2N_3$ requires C, 67·25; H, 9·75; N, 13·1%). The material was insoluble in acid and alkali but on warming with dilute hydrochloric acid, rapid hydrolysis ensued with evolution of carbon dioxide and formation of *cyclo*hexylamine (trinitrotoluene derivative).

3-*Benzyl*-2 : 3-*dihydro*-6-*methyl*-4-*oxo*-2-*phenylimino*-1 : 3-*oxazine* (V; $R^1 = CH_2Ph$, R^2 = Ph).—*N*-Benzyl-*N*′-phenylthiourea (54·5 g.), methyl iodide (35 g.), and ethanol (100 c.c.) were refluxed for 1 hr., and then cooled. A solution of sodium hydroxide (9·25 g.) in water (50 c.c.) was added and solid was deposited (57 g.), m. p. 58—60°. Crystallisation from light petroleum (b. p. 60—80°) gave N-*benzyl*-S-*methyl*-N′-*phenylthiourea* as needles, m. p. 61—62° (Found: N, 10·7. $C_{15}H_{16}N_2S$ requires N, 10·9%). Diketen (17·7 g.) was added during 0·5 hr. to a solution of this thiourea (51 g.) in boiling ethylene dichloride (50 c.c.). After a further 2 hr. for refluxing, methanethiol being evolved, the solvent was removed. Crystallisation of the product from aqueous methanol gave the *oxazine* (V; $R^1 = CH_2Ph$, R^2 = Ph) (45 g., 77%) as needles, m. p. 77° (Found: C, 74·25; H, 5·45; N, 9·45. $C_{18}H_{16}O_2N_2$ requires C, 73·95; H, 5·5; N, 9·6%).

3-*Benzyl*-2 : 3-*dihydro*-6-*methyl*-2 : 4-*dioxo*-1 : 3-*oxazine* (VI; $R^1 = CH_2Ph$).—The oxazine (V; $R^1 = CH_2Ph$, R^2 = Ph) (5·0 g.) was refluxed with concentrated hydrochloric acid (10 c.c.) for 0·5 hr. The solid (2·7 g.) was collected and extracted with hot water, giving the 2 : 4-*dioxo*-1 : 3-*oxazine* (VI; $R^1 = CH_2Ph$) (1·1 g.) [prisms, m. p. 93°, from benzene–light petroleum (b. p. 40—60°)] (Found: C, 66·35; H, 5·35; N, 6·25. $C_{12}H_{11}O_3N$ requires C, 66·35; H, 5·1; N, 6·45%) and a residue of 3-*benzyl*-6-*methyl*-1-*phenyluracil* (1·4 g.) (needles, m. p. 226—227°, from ethanol) (Found: C, 74·0; H, 5·6; N, 9·35. $C_{18}H_{16}O_2N_2$ requires C, 73·95; H, 5·5; N, 9·6%). In a second experiment, the phenylimino-1 : 3-oxazine (5 g.) was refluxed with hydrochloric acid (2 c.c. of acid plus 10 c.c. of water) for 0·75 hr. Isolation as before gave the 2 : 4-dioxo-1 : 3-oxazine (0·36 g.) and the uracil (2·55 g.).

The dioxo-1 : 3-oxazine (0·1 g.) was warmed with aqueous ammonia (*d* 0·88; 5 c.c.), and the solution concentrated and allowed to crystallise, giving 3-benzyl-6-methyluracil as plates, m. p. 198° (Wheeler and McFarland, *loc. cit.*, give m. p. 194°). Similar treatment of the dioxo-1 : 3-oxazine (0·1 g.) with aqueous methylamine (30%; 3 c.c.) gave 3-benzyl-1 : 6-dimethyluracil, m. p. 166—167° (*idem, ibid.*, give m. p. 164°).

Alkaline Hydrolysis of Dioxo-1 : 3-*oxazines* (VI).—(*a*) The oxazine (VI; $R^1 = R^2$ = Ph) (1 g.) was refluxed with a mixture of sodium hydroxide solution (10%; 5 c.c.) and methanol (20 c.c.) for 2 hr. On concentration and cooling of the solution, *NN*′-diphenylurea (0·15 g.), m. p. 246°, was deposited (Young and Clark, *J.*, 1898, 367, give m. p. 238—239°).

(*b*) The oxazine (VI; R^1 = Me, R^2 = Ph) (1 g.) was hydrolysed as above giving *N*-methyl-*N*′-phenylurea (0·35 g.) as plates, m. p. 150° (Dixon, *J.*, 1895, 561, gives m. p. 150·5—151·5°). 3 : 6-Dimethyl-1-phenyluracil (0·15 g.) (see above), m. p. 302°, was also collected from the hot hydrolysis product.

(*c*) The oxazine (VI; $R^1 = CH_2Ph$, R^2 = Ph) (1 g.) was hydrolysed as above, giving *N*-benzyl-*N*′-phenylurea (0·55 g.), m. p. 172° (Ley and Krafft, *Ber.*, 1907, **40**, 703, give m. p. 170°).

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