690. *The Conversion of Sucrose into Pyridazine Derivatives. Part XI. The Ultra-violet Absorption Spectra of Substituted* 1-*Phenyl*-6-*pyridazones and Related Substances.*

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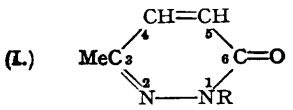
The ultra-violet absorption spectra of a number of derivatives of 3-methyl-1-phenyl-6-pyridazone are reported and the results discussed. Several new compounds of this class of compound are prepared.

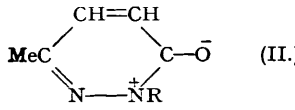
In Parts I and II of this series (*J.*, 1947, 239, 549) the preparation of sulphonamides derived from 6-amino-3-methylpyridazine and 5-amino-3-methyl-1-phenyl-6-pyridazone and of numerous intermediates involved in their synthesis from lævulic acid was described. The preceding paper discussed the ultra-violet absorption spectra of numerous derivatives of 3-methylpyridazine and of 3-methyl-6-pyridazone. In this communication the corresponding data on derivatives of 3-methyl-1-phenyl-6-pyridazone are described. 5-Ethoxy-3-methyl-1-phenyl-6-pyridazone was obtained from the corresponding 4-chloro-derivative (Overend and Wiggins, *J.*, 1947, 549) and ethyl alcoholic potassium hydroxide and gave 5-hydroxy-3-methyl-1-phenyl-6-pyridazone by hydrolysis. 5-Ethoxy-3-methyl-1-*p*-nitrophenyl-6-pyridazone was obtained similarly and by nitration of 5-ethoxy-3-methyl-1-phenyl-6-pyridazone. 1-*p*-Bromophenyl-3-methyl-6-pyridazone was obtained from 1 : 4 : 5 : 6-tetrahydro-6-keto-3-methyl-1-phenylpyridazine (Overend and Wiggins, *loc. cit.*), treatment with bromine effecting both substitution and dehydrogenation. Bromination of 3-methyl-1-phenyl-6-pyridazone gave the same compound, which was also obtained, in poor yield, by the cyclisation of the *p*-bromophenylhydrazone of β-acetylacrylic acid.

3-Methyl-6-pyridazone (I; R = H) exhibits strong absorption with maximum intensity at

2850 A. ($\varepsilon_{max.}$ *ca.* 2000); the maximum is displaced to 3010 A. ($\varepsilon_{max.}$ *ca.* 3000) by alkali (see preceding paper), this band being more sharply defined than that shown by (I; R = H) in neutral solution. 1 : 3-Dimethyl-6-pyridazone (I; R = Me) has a very similar absorption band with peak at 3010 A. ($\varepsilon_{max.}$ *ca.* 2600), so that absorption at about 3000 A. ($\varepsilon_{max.}$ 2500—3000) can be considered as characteristic of the system (I). 3-Methyl-1-phenyl-6-pyridazone (I; R = Ph) shows maximum absorption at 3130 A. ($\varepsilon_{max.}$ *ca.* 6600), *i.e.*, very near to that of (I; R = H or Me).



(I.)



(II.)

In speculating as to the particular electronic transition most likely to be responsible for the afore-mentioned spectra we consider the change (I) $\rightleftharpoons$ (II) as the most likely. In (I; R = Ph) particularly the probability of this is high. The similarity of the spectra of (I; R = H, Me, or Ph) shows that the same electronic transition is operating in all these compounds. When R = Ph, the absorption bands due to the phenyl residue are masked by the more intense absorption of the heterocyclic ring.

Table I presents the absorption data for six derivatives of 3-methyl-1-phenyl-6-pyridazone, differently substituted at position 5. In all of these compounds the absorption is of maximum intensity at approximately 3000 A. with $\varepsilon_{max.}$ *ca.* 6000. [The slight deviation for 5-hydroxy-3-methyl-1-phenyl-6-pyridazone is considered to be due to solvent effects in chloroform (cf. Evans and Wiselogle, *J. Amer. Chem. Soc.*, 1945, **67**, 60).]

TABLE I.

6-Pyridazone derivative.	Concn., mg. %.	Solvent.	γ, A.	$\varepsilon_{max.}$
3-Methyl-1-phenyl-	2·87	EtOH	3130	6500
5-Chloro-3-methyl-1-phenyl-	4·40	EtOH	3190	5900
5-Ethoxy-3-methyl-1-phenyl-	4·58	EtOH	2970	6500
5-Amino-3-methyl-1-phenyl-	4·17	EtOH	3020	6000
5-Acetamido-3-methyl-1-phenyl-	0·60	$CHCl_3$	3090	5000
5-Hydroxy-3-methyl-1-phenyl-	5·40	$CHCl_3$	3350	5200
1-*p*-Bromophenyl-3-methyl-	4·02	EtOH	3150	7900

When a bromine atom is introduced into the *para*-position of the phenyl residue there is a very slight increase in both the wave-length of maximum absorption and in the intensity (see Table I). The same effect is observed for benzene and bromobenzene ($\lambda_{max.}$ 2590 A., $\varepsilon_{max.}$ *ca.* 200, and $\lambda_{max.}$ 2640 A., $\varepsilon_{max.}$ *ca.* 300, respectively). If in 3-methyl-1-phenyl-6-pyridazone and its 5-chloro-, 5-ethoxy-, 5-amino-, and 5-acetamido-derivatives the phenyl residue is substituted in the *para*-position by a nitro-group, the position of maximum absorption is displaced towards the visible region of the spectrum and the intensity is also increased (see Table II) (for the chloro-compound a band at a lower wave-length, absent in the other derivatives, became measurable).

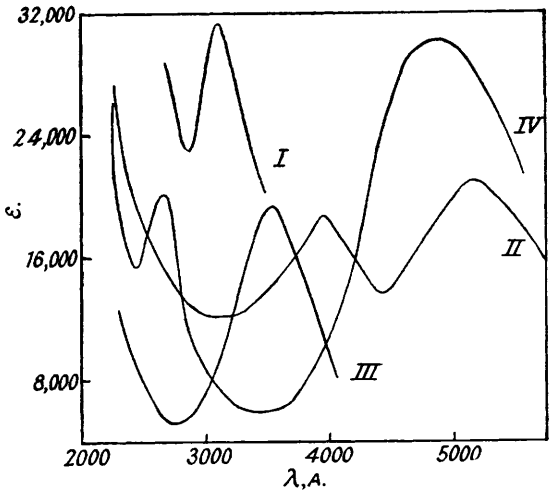
TABLE II.

6-Pyridazone derivative.	Concn., mg. %.	Solvent.	λ, A.	$\varepsilon_{max.}$
3-Methyl-1-*p*-nitrophenyl-	3·63	EtOH	3270	9000
5-Chloro-3-methyl-1-*p*-nitrophenyl-	3·10	EtOH	2440 3300	11,000 10,000
5-Ethoxy-3-methyl-1-*p*-nitrophenyl-	3·04	EtOH	3200	9000
5-Amino-3-methyl-1-*p*-nitrophenyl-	2·60	EtOH	3250	6300
5-Acetamido-3-methyl-1-*p*-nitrophenyl-	2·66	EtOH	3240	8500

The absorption spectra were also measured of the reduced derivatives, 1 : 4 : 5 : 6-tetrahydro-6-keto-3-methyl-1-phenyl- and 3-methyl-1-*p*-nitrophenylpyridazine. The former in alcohol solution showed maximum absorption of light at 2370 A. ($\varepsilon_{max.}$ 11,000) and the latter at 3220 A. ($\varepsilon_{max.}$ 7400). The spectrum of the latter compound undergoes a remarkable change when its solution is made alkaline, absorption occurring in the visible region (*e.g.*, $\lambda_{max.}$ 3920 and 5020 A., $\varepsilon_{max.}$ 10,900 and 11,500 respectively). Neither 3-methyl-1-phenyl-6-pyridazone nor its tetrahydro-derivative shows such a change. The change may be due to 1 : 4 : 5 : 6-tetrahydro-6-keto-3-methyl-1-*p*-nitrophenylpyridazine being partly converted into lævulic acid *p*-nitrophenylhydrazone

(Fischer and Ach, *Annalen*, 1889, **253**, 57). Trial experiments showed that potassium lævulate hydrazone was formed when 1 : 4 : 5 : 6-tetrahydro-6-keto-3-methylpyridazine was treated with potassium hydroxide. The absorption spectrum of lævulic acid *p*-nitrophenylhydrazone in both neutral and alkaline solution is shown in the figure.

Absorption spectra.



I, 3-*Methyl*-1-p-*nitrophenyl*-6-*pyridazinone* (c, 1·02 *mg.* % *in* EtOH).
II, *as* I, *but in* EtOH + 0·1 *c.c. of* 5N-NaOH *per l.*
III, *Lævulic acid* p-*nitrophenylhydrazone* (c, 1·55 *mg.* % *in* EtOH).
IV, *as* III, *but in* EtOH + 0·1 *c.c. of* 5N-NaOH *per l.*

It is of some importance to account for the difference in the absorption spectrum of 1 : 4 : 5 : 6-tetrahydro-6-keto-3-methyl-1-phenylpyridazine and that of the dehydrogenated product 3-methyl-1-phenyl-6-pyridazone. The former shows a maximum absorption at 2370 A. ($\varepsilon_{max.}$ 11,000) and in this respect is very similar to lævulic acid phenylhydrazone, whereas the latter absorbs most strongly at 3130 A. ($\varepsilon_{max.}$ 6500). These values may be indicative of the change from a phenylhydrazone of lævulic acid cyclised by no more than a lactam linkage into a resonance-stabilised heterocyclic system. This increase in stability (resonance) of 3-methyl-1-phenyl-6-pyridazone is demonstrated by the shift of the absorption band of 1 : 4 : 5 : 6-tetrahydro-6-keto-3-methyl-1-phenylpyridazine from 2370 A. to longer wave-lengths. Simultaneously a lowering in the intensity of the absorption occurs, a change which generally takes place when the resonance of an absorbing system is increased. This effect is masked in the case of 3-methyl-1-*p*-nitrophenyl-6-pyridazone and the corresponding tetrahydro-derivative by the powerfully absorbing nitro-group, but even in this case there is a slight increase in the wave-length of maximum absorption on passing from the tetrahydro-6-ketopyridazine to the 6-pyridazone derivative, although the intensity change does not follow the normal course.

Experimental.

5-Ethoxy-3-methyl-1-phenyl-6-pyridazone.—To 5-chloro-3-methyl-1-phenyl-6-pyridazone (0·44 g.) (Overend and Wiggins, *J.*, 1947, 549) in ethyl alcohol (5 c.c.), potassium hydroxide (1 mol., 0·12 g.), also dissolved in alcohol (5 c.c.), was added and the whole was heated under reflux for 0·5 hour, solid potassium chloride separating. The solution was evaporated to dryness and the residue extracted with water to remove inorganic materials. The *ethoxy*-derivative, recrystallised from alcohol, formed colourless plates (0·16 g., 35·5%), m. p. 144—145° (Found : C, 67·3; H, 6·3; N, 11·7. $C_{13}H_{14}O_2N_2$ requires C, 67·7; H, 6·1; N, 12·1%).

5-Hydroxy-3-methyl-1-phenyl-6-pyridazone.—5-Ethoxy-3-methyl-1-phenyl-6-pyridazone (0·40 g.) and concentrated hydrochloric acid (10 c.c.) were heated together in a sealed tube at 130° for 4 hours. After being cooled the solution was evaporated to dryness and the residue washed with water and then dissolved in cold dilute aqueous sodium carbonate. The *hydroxy*-compound, precipitated by addition of hydrochloric acid and recrystallised from aqueous alcohol, formed white needles (quantitative yield), m. p. 200° (Found : C, 64·9; H, 5·4. $C_{11}H_{10}O_2N_2$ requires C, 65·3; H, 5·0%).

5-Ethoxy-3-methyl-1-p-nitrophenyl-6-pyridazone.—(*a*) 5-Chloro-3-methyl-1-*p*-nitrophenyl-6-pyridazone (0·47 g.) was dissolved in alcohol (50 c.c.), and potassium hydroxide (1 mol., 0·1 g.) added. The mixture

was heated under reflux for 0·5 hour and then evaporated to dryness. The inorganic material was extracted with water and the residue recrystallised from aqueous alcohol, forming yellow crystals (0·35 g., 73%) of the 5-*ethoxy*-derivative, m. p. 138° (Found: C, 56·4; H, 4·7. $C_{13}H_{13}O_4N_3$ requires C, 56·7; H, 4·8%).

(*b*) 5-Ethoxy-3-methyl-1-phenyl-6-pyridazone (0·045 g.) was added to fuming nitric acid (10 c.c.), cooled to 0°. The mixture was left at 0° for 1 hour, then poured into water, and the product extracted with benzene. After being dried, the solvent was removed by evaporation and the residual syrup induced to crystallise. After recrystallisation from aqueous alcohol, the product had m. p. 137—138° alone or on admixture with the above specimen. The yield was quantitative.

1-p-*Bromophenyl*-3-*methyl*-6-*pyridazone*.—(*a*) A solution of 1 : 4 : 5 : 6-tetrahydro-6-keto-3-methyl-1-phenylpyridazine (3·76 g.) in dry acetic acid (50 c.c.) was cooled to 0° and bromine (2·06 c.c.) slowly added. 1-p-*Bromophenyl*-3-*methyl*-6-*pyridazone* which separated was washed with glacial acetic acid and recrystallised from aqueous acetic acid as flocculent white needles, m. p. 72—73° (Found: C, 49·7; H, 3·9. $C_{11}H_9ON_2Br$ requires C, 49·8; H, 3·4%).

(*b*) To 6-methyl-2-phenyl-3-pyridazone (3·0 g.) in dry acetic acid (20 c.c.), bromine (0·84 c.c.) was slowly added at room temperature. After evaporation, the residue distilled at 199—200° (bath-temp.)/0·005 mm., as a colourless syrup, $n^{22\cdot5}$ 1·6109. The bromo-derivative, recrystallised first from aqueous alcohol and then from light petroleum, formed colourless cubes, m. p. 73—74°. Its alcoholic solution exhibited a green fluorescence in ultra-violet light.

β-Acetylacrylic Acid p-*Bromophenylhydrazone*.—β-Acetylacrylic acid (2·0 g.) in water (7 c.c.) was mixed with *p*-bromophenylhydrazine (3·3 g.) in glacial acetic acid (10 c.c.), and sufficient alcohol added to make the mixture homogeneous. The mixture was then warmed. On cooling, *β-acetylacrylic acid* p-*bromophenylhydrazone* (4·4 g., 88%) separated; crystallised from aqueous alcohol, this had m. p. 167—170° (Found: C, 46·3; H, 4·2. $C_{11}H_{11}O_2N_2Br$ requires C, 46·6; H, 3·9%).

Cyclisation of β-Acetylacrylic Acid p-*Bromophenylhydrazone*.—The above hydrazone (5·0 g.) was heated at 120° under diminished pressure for 2 hours. After being cooled the solid recrystallised from light petroleum in colourless cubes. It was 2-*p*-bromophenyl-6-methyl-3-pyridazone (1·47 g., 32%), m. p. 73—74°.

Treatment of 1 : 4 : 5 : 6-*Tetrahydro*-6-*keto*-3-*methylpyridazine with Potassium Hydroxide*.—When the anhydrous ketone (2 g.) and potassium hydroxide (2 g.) in alcohol (10 c.c.) were kept overnight, a thick mat of needles separated. These were collected (2·1 g.) as very deliquescent crystals of indefinite m. p., which contained nitrogen and potassium. They were probably potassium lævulate hydrazone (Found: K, 23·7. Calc. for $C_5H_9O_2N_2K$: K, 23·2%).

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