The Photochemistry of 2,3-Dimethyl-1-phenyl-3-pyrazolin-5-one

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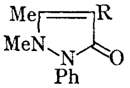
RECENT investigations of the photochemistry of heterocyclic compounds including pyrazole,[1] thiophen,[2] and isoxazole[3,4] derivatives, all of which are pseudo-aromatic in character, have shown that rearrangements involving transposition of the ring atoms occur as the common mode of reaction. Experiments in this laboratory with 2,3-dimethyl-1-phenyl-3-pyrazolin-5-one (antipyrine, Ia) and those by Reisch[5,6] with a derivative (Ib) of this compound demonstrate that a similar rearrangement takes place in the non-aromatic pyrazolone system.

Irradiation of antipyrine in methanol with a Hanovia 450w medium-pressure arc lamp for 70 hr. leads to the formation of a dark-coloured, vile-smelling solution from which five products and unchanged antipyrine (50%) were isolated by chromatography on silica. The three minor products (about 5% total yield) were identified as the known compounds, methyl phenylcarbamate, *N*-methyl-*N'*-phenyloxamide, and oxanilide, by comparison of their melting points and infrared spectra with those of synthetic samples.

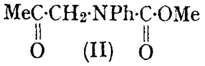
The major product (20% yield) was an oil, shown by analysis to have the empirical formula $C_{11}H_{13}NO_3$, and which gave positive iodoform and 2,4-dinitrophenylhydrazine tests. The infrared spectrum ($CHCl_3$) of this compound showed carbonyl stretching frequencies at 1700 and 1745 cm.$^{-1}$. Its n.m.r. spectrum had bands at $\delta(CCl_4)$ 2·05 (3H, singlet), 3·56 (3H, singlet), 4·25 (2H, singlet), and 7·20 (5H, singlet) p.p.m. The photo-product was assigned structure (II) on the basis of this information.

The other photo-product obtained in 10% yield was a crystalline solid, m.p. 134—135°, which on standing in benzene, chloroform, or carbon tetrachloride, was converted into a gummy solid from which 1,5-dimethyl-3-phenylhydantoin (III),[7] m.p. 146—146·5°, identified by analysis, by its infrared spectrum ($CHCl_3$) which had carbonyl bands at 1720 and 1780 cm.$^{-1}$, and by its n.m.r. spectrum with peaks at $\delta(CDCl_3)$ 1·48 (3H, doublet, J = 7 c./sec.), 3·00 (3H, singlet), 4·00 (1H, quartet, J = 7 c./sec.) and 7·40 (5H, singlet) p.p.m., could be isolated. The original, solid photo-product was shown to be isomeric with antipyrine by analysis. Its infrared spectrum ($CHCl_3$) showed carbonyl absorption at 1680 cm.$^{-1}$. The n.m.r. spectrum of the compound was similar to that of antipyrine except for downfield shifts of the positions of the *N*-methyl (δ 3·20) and vinyl protons (δ 6·30), and the change of the phenyl singlet to a multiplet. The weak coupling between the vinyl methyl and the vinyl proton seen as a broadening of those peaks in the spectrum of antipyrine was also visible in the spectrum of the photo-product. The compound is therefore assigned the imidazolinone structure (IV), which is, apparently, readily converted into the hydantion (III) by air oxidation.

Reisch has reported[5] the formation of an imidazolinone derivative upon the irradiation of amidopyrine (Ib) in methanol or ethanol, while in benzene he observed[6] products derived from fragmentation of the ring. A similar dependence of the nature of the products on solvent has been observed in this laboratory. Preliminary studies indicate that irradiation of antipyrine in ethanol gives the same products as isolated from its reaction in methanol except that ethyl phenylcarbamate and the corresponding *N*-substituted compound analogous to (II) are obtained. No imidazolinone (IV) is formed when the irradiation is carried out in benzene, and it is formed in low yield in acetone, where the major product is an oil which has infrared absorption ($CHCl_3$) at 1675 and 1740 cm.$^{-1}$, and bands in the n.m.r. at $\delta(CCl_4)$ 2·10 (3H, singlet), 4·40 (2H, singlet), 7·18 (5H, multiplet), and 8·35 (1H, singlet) p.p.m. This evidence leads to the assignment of structure (V), an *N*-substituted formanilide, to this photo-product.

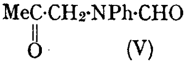


(Ia) R=H
(Ib) R=NMe_2



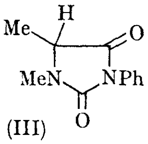
$$\mathrm{Me}\underset{\overset{\|}{\mathrm{O}}}{\mathrm{C}}\cdot\mathrm{CH_2}\cdot\mathrm{NPh}\cdot\underset{\overset{\|}{\mathrm{O}}}{\mathrm{C}}\cdot\mathrm{OMe}$$

(II)

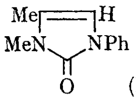


$$\mathrm{Me}\underset{\overset{\|}{\mathrm{O}}}{\mathrm{C}}\cdot\mathrm{CH_2}\cdot\mathrm{NPh}\cdot\mathrm{CHO}$$

(V)



(III)



(IV)

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