

THE ACTION OF LIGHT ON 4-AMINO-3-PYRAZOLIN-5-ONE DERIVATIVES
IN WATER ⁺

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As has already been shown (1, 2), the products formed by the action of light on 4-amino-3-pyrazolin-5-one derivatives are solvent dependent. This was recently confirmed by E ğ e (3) in his report on the irradiation of 2,3-dimethyl-1-phenyl-3-pyrazolin-5-one (antipyrine) (IIa) in methanol, ethanol, acetone, and benzene. The stability of aqueous solutions of 3-pyrazolin-5-one is especially interesting from the pharmaceutical standpoint (4). Herein is reported briefly results obtained concerning the question of stability towards light.

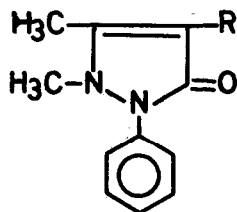
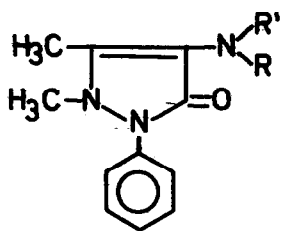
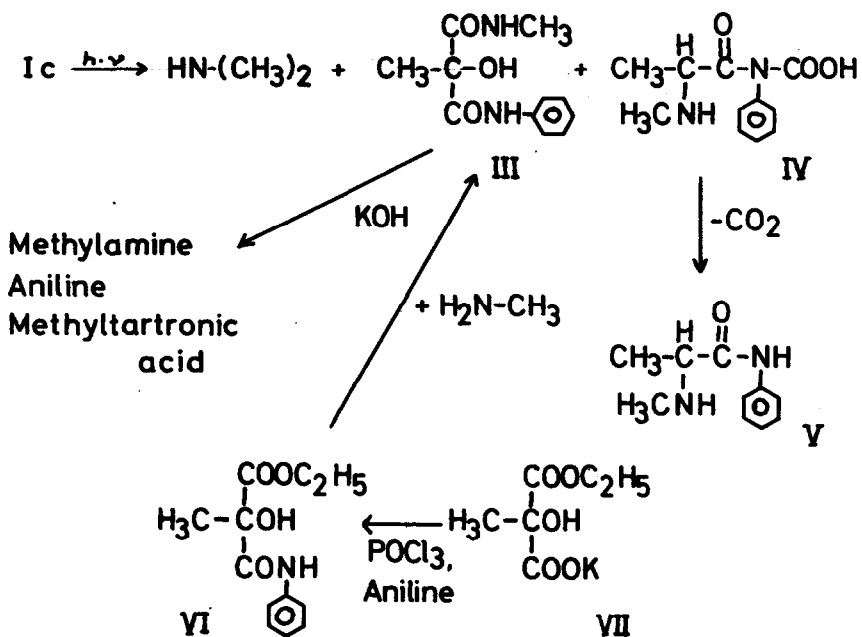
If one, for example, irradiates a suspension of 50 g of amidopyrine (Ic) in 500 ml of water for 100 hrs. with a mercury high-pressure immersion arc lamp ⁺⁺ (water-cooled to 18-20^o), one obtains in addition to dimethylamine two further products. The one could be extracted with ether (substance A), and the other (substance B) was obtained by concentration of the ether

extracted water solutions. Substance A (m. p. 110° , H_2O , resp., toluene, yield 60%) has, according to the analysis and mass spectrum (m/e 222) the formula $C_{11}H_{14}N_2O_3$.

Vigorous saponification of A with methanolic potassium hydroxide in a reaction bomb at 100° for 4 hrs. yielded in addition to methylamine and aniline, methyltartronic acid. These products were identified by comparison with authentic samples. This decomposition together with the n. m. r., i. r., and mass spectrum led to III as a possible structure for A. This structure was confirmed by synthesis of the compound from methyltartronic acid diethylester (5), as shown in fig. I.

The substance B which is very water soluble is an acid ($C_{11}H_{14}N_2O_3$, m. p. 165° (decomp.), ethanol/water). When B was heated above its melting point, decarboxylation took place with formation of 2-N-methylaminopropionic acid anilide (V) (comparison with an authentic sample (2)). On the basis of this decarboxylation and the n. m. r., and i. r. spectrum B was assigned the structure IV.

Aqueous solutions of Ia, Ib, and Id on irradiation form the corresponding amines ($HN \begin{smallmatrix} R' \\ R \end{smallmatrix}$) and likewise the photoproducts III and IV. The formation of IIb as an intermediate could be shown by thin-layer chromatography. Complete details of the experiments carried out, of the reaction mechanism and of the products resulting from the use of other solvents will be reported at a later date.

Ia $R + R' = H$ IIa $R = H$ (Antipyrine)Ib $R = CH_3$, $R' = H$ IIb $R = OH$ Ic $R + R' = -CH_3$ (Amidopyrine)Id $R = CH_3$, $R' = -CH_2-SO_3Na$ (Dipyron)

L I T E R A T U R

- +) Part III in the series: Studies on Irradiation Chemistry
Part II: see reference (2)
- ++) Immersion lamp TQ 120K with pyrex cooler, Quarzlampengesellschaft mbH, Hanau
- (1) J. Reisch, Pharmazie, 1966, 21, 183
- (2) J. Reisch, Bull. chim. Therapeut., 1966, 355
- (3) S.N. Ege, Chem. Commun., 1967, 488
- (4) J. Reisch, Dtsch. Apotheker-Ztg., 1965, 105, 1524
- (5) S. Eskola and V. Muotinen, Suomen Kemistilehti, 1947, 20B, 16;
C.A. 1948, 42, 122