A Photochemical Reaction of Pyridazine *N*-Oxides

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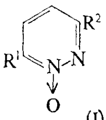
PHOTOREARRANGEMENT of aromatic *N*-oxides and nitrones has been described by various workers.[1] We now report a novel photochemical reaction of pyridazine *N*-oxides involving hydroxymethylation on pyridazine nucleus and deoxygenation.

Irradiation of a methanol solution of pyridazine *N*-oxide derivatives[2–5] (Ia—e) through Pyrex glass with high-pressure mercury arc lamp under argon atmosphere at room temperature gave the corresponding deoxygenated products[6–8] (IIa—e) and hydroxymethyl derivatives (IIIa, c, d and IIIe) as shown in the Table. In the case of (Ia) and (Ie), there was obtained, in addition to the major products, the corresponding isomeric compounds [(IVa) and (IVe)] in low yield.

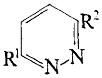
The n.m.r. spectrum (perdeuteriodimethyl sulphoxide) of (IIIa) [$C_6H_7N_2OCl$, m.p. 184·5—186°, ν_{max} (Nujol) 3120 cm.$^{-1}$] shows proton signals at τ 2·34 (1H, singlet, pyridazine ring proton), τ 4·30 (1H, broad triplet, OH, disappeared upon addition of D_2O), τ 5·49 (2H, broad doublet, $-CH_2O-$, broad singlet upon addition of D_2O) and τ 7·40 (3H, singlet, Me). Oxidation of (IIIa) with potassium dichromate in sulphuric acid afforded a carboxylic acid (V) [m.p. 181° (decomp.)], which was proved to be identical with 6-chloro-3-methylpyridazine-5-carboxylic acid derived from known 1,6-dihydro-3-methyl-6-oxopyridazine-5-carboxylic acid[9] and phosphorous oxychloride. From these facts, the structure of 6-chloro-5-hydroxymethyl-3-methylpyridazine was assigned to (IIIa).

The n.m.r. spectrum ($CDCl_3$) of (IVa) ($C_5H_5N_2OCl$, m.p. 102—104°, ν_{max} (Nujol) 3240 3150, 1674 cm.$^{-1}$) shows proton signals at τ 3·29 (1H, singlet, ring proton), τ 7·49 (3H, singlet, $COMe_3$). From the spectral and analytical data, the structure of (IVa) was considered to be 3-acetyl-5-chloropyrazole.

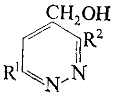
The n.m.r. spectrum (perdeuteriodimethyl sulphoxide) of photoproduct (IIIc) [$C_7H_{10}N_2O$, m.p. 136—137°, ν_{max} (Nujol) 3100 cm.$^{-1}$] shows proton signals at τ 2·57 (1H, singlet, pyridazine ring proton), τ 4·54 (1H, broad multiplet, OH, disappeared upon addition of D_2O), τ 5·49 (2H, broad doublet, $-CH_2O-$), τ 7·43 (3H, singlet, Me) and τ 7·52 (3H, singlet, Me). From these data, the structure 4-hydroxymethyl-3,6-dimethylpyridazine was assigned to (IIIc). Photoproduct (IIId) ($C_6H_8N_2O$, m.p. 78—79°) was proved to be identical with 5-hydroxymethyl-3-methylpyridazine, derived from (IIIa) by catalytic hydrogenation with palladium–charcoal in aqueous methanolic ammonia, and photoproduct (IIIe) ($C_7H_{10}N_2O_2$, m.p. 153—155°) was identical with 5-hydroxymethyl-3-methyl-6-methoxypyridazine derived from (IIIa) by treatment with sodium methoxide.



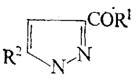
(I)



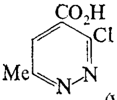
(II)



(III)



(IV)



(V)

a: R^1 = Me, R^2 = Cl
b: R^1 = R^2 = H
c: R^1 = R^2 = Me
d: R^1 = Me, R^2 = H
e: R^1 = Me, R^2 = OMe

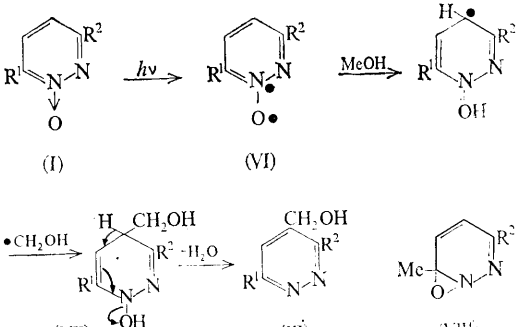
TABLE

Photoinduced reaction products of pyridazine N-*oxide derivatives*

Starting materials	Products
(Ia)[2]	(IIa)[6] (25·3%), (IIIa) (7·0%), (IVa) (0·2%)
(Ib)[3]	(IIb) (6·2%), recovery (Ib) (21·3%)
(Ic)[4]	(IIc)[7] (10·9%), (IIIc) (0·5%)
(Id)[2]	(IId)[8] (18·9%), (IIId) (0·02%)
(Ie)[5]	(IIe)[6] (9·0%), (IIIe) (1·1%), (IVe) (0·2%)

The n.m.r. spectrum ($CDCl_3$) of photoproduct (IVe) [$C_6H_8N_2O_2$, m.p. 89—90°, ν_{max} (Nujol 3220, 3160, 1669 cm.$^{-1}$)] shows proton signals at τ 3·85 (1H, singlet, ring proton), τ 6·07 (3H, singlet, –OMe) and τ 7·53 (3H, singlet, COMe). From these data, the structure of (IVe) was assigned to 3-acetyl-5-methoxypyrazole.

A possible mechanism for the hydroxymethylation of pyridazine *N*-oxides involves initial excitation of the *N*-oxides to the excited-state species represented by (VI), followed by abstraction of a hydrogen atom from methanol to give, after combination of radical, the intermediate (VII). This intermediate undergoes decomposition by way of the Scheme shown. As for the photochemical deoxygenation of aromatic *N*-oxides in solution, there has been a report on the reaction of purine *N*-oxides.[10] However the reaction mechanism is not clear at present.



(I) (VI) (VII) (III) (VIII)

The formation of the pyrazole derivatives probably proceeds through an oxaziran intermediate (VIII) as demonstrated in quinoline *N*-oxides[11] and pyridine *N*-oxides.[12]

The authors are grateful to Professor Emeritus E. Ochiai of the University of Tokyo and to Dr. K. Takeda, Director of this laboratory, for their interest and encouragement on this work. Thanks are also due to Mr. H. Matsumoto for his technical assistance.

(*Received, October 3rd*, 1967; *Com.* 1051.)

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