Photochemical Formation of Azo-compounds from 1-Phenylpyrazolones

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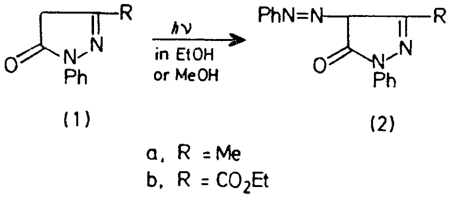
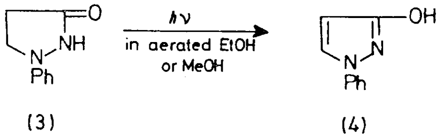
Summary 1-Phenylpyrazolones in alcoholic media form photochemically the corresponding azo-compounds by an intermolecular reaction between the ground state of (**1**) and the diazonium ion (**9**).

It is well known that the five-membered nitrogen heteroaromatic compounds undergo interesting photochemical reactions such as decomposition, isomerization, and ring expansion.[1] However, no photochemical formation of azo-compounds has been reported.



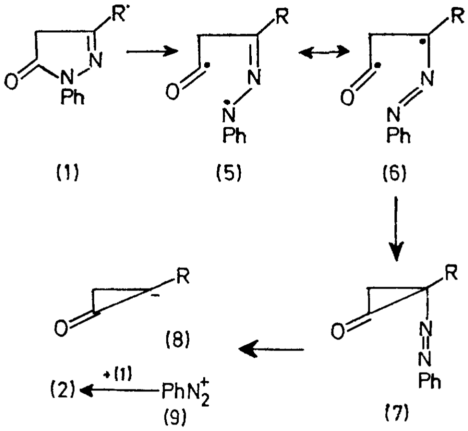
Scheme 1

We have found a new photochemical reaction of 1-phenylpyrazolones which yields azo-compounds as the main products (Scheme 1). For example, irradiation of a 10^{-2} M ethanolic solution of the 3-methyl compound (**1a**) for 12 h at 254 nm gave the azo-compound (**2a**) as the major photoproduct (yield: *ca.* 10%) after chromatography in benzene over silica gel and recrystallization from ethanol. Compound (**2a**) had analytical and spectral (i.r., u.v., n.m.r., and mass) data and m.p. identical with those of an authentic sample prepared by the usual method. The ethoxycarbonyl compound (**1b**) similarly gave (**2b**) in



Scheme 2

ca. 6% yield after irradiation for 18 h. These photochemical reactions occurred both in aerated and degassed alcoholic media.



SCHEME 3

In contrast, 10^{-2} M of an ethanolic solution of the pyrazolidinone (**3**) at 254 nm gave the 3-hydroxy-pyrazole (**4**), which was identical with an authentic sample (see Scheme 2). In degassed media, photochemical dehydrogenation of (**3**) did not take place, and an ethanolic solution of (**3**) was photostable at 254 nm [disappearance quantum yield of (**3**) $< 10^{-6}$]. Thus, photochemical oxidation occurs in the presence of oxygen when the pyrazoline bears a carbonyl group in the 3-position.

The photochemical formation of azo-compounds from (**1**) seems to proceed *via* a Norrish type I fission (α-cleavage)[2] and subsequent reactions (Scheme 3).

Irradiation of a 0·1M ethanolic solution of (**1b**) in the presence of 2-naphthol (0·1M) as an azo-coupling reagent at 254 nm for 4 days gave the azo-compound of 2-naphthol (yield: *ca.* 0·5%), showing that the intermediate (**7**) dissociates into the ionic species (**8**) and (**9**), and the ground state of (**1**) reacts intermolecularly with the diazonium ion (**9**). Of course, formulation of the presence of the anionic species (**8**) is purely tentative. The quantum yields for the product formation, Φ(**2**), depended upon the initial concentration of (**1**) [*e.g.* Φ(**2a**) $1{\cdot}5 \times 10^{-4}$ (10^{-2}M) and $7{\cdot}0 \times 10^{-5}$ (10^{-4}M); Φ(**2b**) $7{\cdot}7 \times 10^{-5}$ ($0{\cdot}8 \times 10^{-2}$M) and $5{\cdot}0 \times 10^{-6}$ ($0{\cdot}8 \times 10^{-4}$M), where the figures in parentheses refer to the starting concentration of (**1**)]. The effect of dissolved oxygen on Φ(**2**) was negligible.

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[1] O. L. Chapman, Ed., 'Organic Photochemistry', Vol. 2 Marcel Dekker, New York, 1967 p. 117; 'Methoden der Organischen Chemie,' Ed. E. Müller, Band IV/5a, Photochemie, Teil I, Georg Thieme Verlag Stuttgart, 1975, p. 546.

[2] K. Tsutsumi, K. Matsui, and H. Shizuka, *Mol. Photochem.*, in the press.