[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, FACULTY OF SCIENCE, CAIRO UNIVERSITY]

# Photochemical Reactions in Sunlight. Experiments with 2-*N*-Phenyl-α,β-naphtho-1,2,3-triazolequinone and Monoxime Derivative in Sunlight and in Dark

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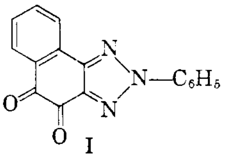
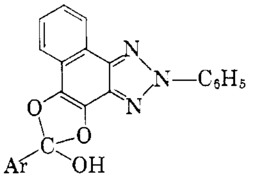
The photochemical addition of aldehydes to heterocyclic nitrogen *o*-quinones, such as 2-*N*-phenyl-α,β-naphtho-1,2,3-triazolequinone (I), has now been investigated and the photoproducts (IIa–b) are obtained. The oxazole (Va) has been obtained either by heating the photoproduct of the reaction of 2-*N*-phenyl-α,β-naphtho-1,2,3-triazolequinone monoxime (IV) and *p*-methoxybenzaldehyde and/or by allowing IV to react with the aldehyde in the dark in the presence of piperidene. The photochemical addition of I to olefins, e.g., stilbene and benzalphthalide, has been investigated and the photoproducts VI and VII are obtained respectively.

In continuation of our previous work, the action of aromatic aldehydes on heterocyclic nitrogen *o*-quinones has been extended.[1-3]

We now have allowed the orange 2-*N*-phenyl-α,β-naphtho-1,2,3-triazolequinone (I) to react with aromatic aldehydes, namely, *p*-methoxybenzaldehyde and 3,4-diethoxybenzaldehyde, in the absence of oxygen and have found that addition takes place in molecular proportions. The colorless photoproducts (IIa–b) are obtained in good yield in most cases and separate during exposure. It is believed that these photoproducts have constitutions such as II or the corresponding open form.

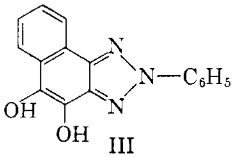


I



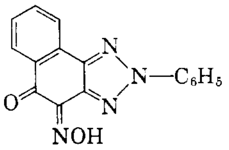
IIa, Ar = $p$-$CH_3OC_6H_4$
b, Ar = 3,4-diethoxyphenyl

Compound IIa is colorless, insoluble in cold aqueous sodium hydroxide solution, and gives no color with ferric chloride. It yields *p*-methoxybenzoic acid and I on heating with concentrated hydrochloric acid in acetic acid. The formation of I may be attributed to the ready oxidation of the intermediate hydroquinone (III) by atmospheric oxygen.[4]

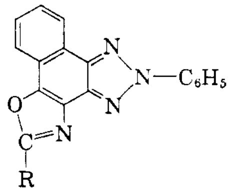


III

*2-N-Phenyl-α,β-naphtho-1,2,3-triazolequinone monoxime and aromatic aldehydes.* While the mechanism of the action of aromatic aldehydes on *o*-quinone monoximes is not known, the over-all results may be summarized: The oxime (IV or isomer) and *p*-methoxybenzaldehyde do not react in benzene in the dark at room temperature; in sunlight, however, a product was obtained which on heating yielded the corresponding oxazole (Va or isomer).[3,5]



IV (or isomer)



V (or isomer)
Va, R = $p$-$CH_3OC_6H_4$
b, R = 3,4-diethoxyphenyl

We have also investigated the action of aromatic aldehydes, *e.g.*, *p*-methoxybenzaldehyde and 3,4-diethoxybenzaldehyde, on IV and have found that the corresponding oxazoles (Va–b) are formed when the reactants are heated without a solvent in the presence of piperidine.

*2-N-Phenyl-α,β-naphtho-1,2,3-triazolequinone and ethylenes.* In an extension of our previous work on the action of ethylenes on *o*-quinones in sunlight,[3,6,7]

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(1) A. Mustafa, A. H. Harhash, A. K. Mansour, and S. M. Omran, *J. Am. Chem. Soc.*, **78**, 4306 (1956).

(2) A. Schönberg, A. Mustafa, and S. M. Zayed, *J. Am. Chem. Soc.*, **75**, 4302 (1953).

(3) A. Mustafa, A. K. Mansour, and A. F. Shalaby, *J. Am. Chem. Soc.*, **81**, 3409 (1959).

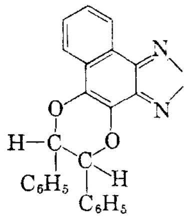
(4) G. Charrier and A. Manfredi, *Gazz. chim. ital.*, **56**, 196–207 (1926); *Chem. Abstr.*, **20**, 2859 (1926).

(5) This reaction is similar to the formation of 2-phenylphenanthroxazole by the action of heat on the product obtained by exposing a mixture of phenanthraquinone monoxime and benzaldehyde to sunlight: *cf.* A. Schönberg *et al.*, *J. Chem. Soc.*, 374 (1950).

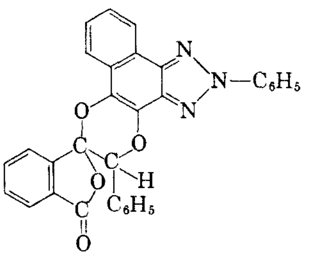
(6) A. Schönberg, A. Mustafa, and co-workers, *J. Chem. Soc.*, 387 (1944); 551 (1945), 2126 (1948); *Chem. Revs.*, **40**, 190 (1948); A. Mustafa and A. M. Islam, *J. Chem. Soc.*, S81 (1949); A. Mustafa, *J. Chem. Soc.*, S83 (1949); 1034 (1951).

(7) For the mechanism of such photo-additions (*cf.* G. O. Schenk, *Naturwissenschaften*, **40**, 229 (1953); G. O. Schenk and G. A. Schmidt Thomee, *Ann.*, **584**, 199 (1953), and A. Schönberg *et al.*, *J. Am. Chem. Soc.*, **77**, 3850 (1955); *cf.* also *Preparative Organische Photochemie*, A. Schönberg, Springer-Verlad, Berlin, Göttingen, Heil Heidelberg, 1958, p. 93.

we now have studied the action of stilbene and/or benzalphthalide on I and have found that, whereas no reaction takes place in the dark, in sunlight colorless products VI and VII or isomer are formed. Compound VI regenerated the starting materials on heating.



VI



VII (or isomer)

## EXPERIMENTAL

*Preparation of 2-N-phenyl-α,β-naphtho-1,2,3-triazolequinone* (I). The quinone was prepared according to the procedure described by Charrier and Manfredi,[4] in 35% yield, m.p. 207–209°.

*Photochemical reactions with 2-N-phenyl-α,β-naphtho-1,2,3-triazolequinone in sunlight.*[7a] *General remarks.* The photochemical reactions were carried out as described in the previous publications.[3]

*Photochemical reaction of 2-N-phenyl-α,β-naphtho-1,2,3-triazolequinone with p-methoxybenzaldehyde.* A mixture of the quinone (0.8 g.) and *p*-methoxybenzaldehyde (0.7 g.) in benzene (35 ml.) was exposed to sunlight for 7 days (December). The photoproduct (IIa) separated during irradiation as almost colorless crystals. Recrystallization from xylene gave colorless crystals, m.p. 227–228°. Yield ca., 76%.

*Anal.* Calcd. for $C_{24}H_{17}N_3O_4$: C, 70.07; H, 4.13; N, 10.12. Found: C, 69.79; H, 4.13; N, 10.07.

IIa is insoluble in aqueous sodium hydroxide solution and gives no color with ferric chloride.

*Photochemical reaction of* I *and 3,4-diethoxybenzaldehyde.* A mixture of the quinone I (0.7 g.) and 3,4-diethoxybenzaldehyde (0.9 g.) in benzene (40 ml.) was exposed to sunlight for 10 days (December). The photoproduct (IIb), separated during irradiation as almost colorless crystals. It was filtered and recrystallized from xylene as colorless crystals, m.p. 230°. Yield ca. 80%.

*Anal.* Calcd. for $C_{27}H_{23}N_3O_6$: C, 69.08; H, 4.90; N, 8.95. Found: C, 69.22; H, 4.76; N, 8.52.

IIb is insoluble in aqueous sodium hydroxide solution; it gives a yellow color with concd. sulfuric acid and develops no color with ferric chloride.

*Action of hydrochloric acid on* IIa. To a solution of 0.5 g. of IIa in 30 ml. of glacial acetic acid, was added 3 ml. of concd. hydrochloric acid. The reaction mixture was refluxed for 5 hr., cooled and poured into water. It was then neutralized with sodium bicarbonate solution and allowed to stand overnight. The orange residue formed was collected and crystallized from acetic acid. It was identified as the quinone (I) (m.p. and mixed m.p.). Acidification of the alkaline filtrate yielded *p*-methoxybenzoic acid (m.p. and mixed m.p.).

*Photochemical reaction of* I *with stilbene.* A mixture of the quinone (0.9 g.) and stilbene (0.8 g.) in benzene (35 ml.) was exposed to sunlight for 7 days (December). The photoproduct (VI) separated as almost colorless crystals during exposure to sunlight. It was collected and recrystallized from benzene as almost colorless crystals, m.p. 253–254°. Yield ca., 82%.

*Anal.* Calcd. for $C_{30}H_{21}N_3O_2$: C, 79.12; H, 4.39; N, 9.23. Found: C, 79.31; H, 4.46; N, 9.05.

VI is insoluble in aqueous sodium hydroxide solution and gives no color with ferric chloride.

*Thermal decomposition of* VI. VI (0.2 g.) was heated at 265–270° (bath temperature) for 1 hr. under reduced pressure. The colorless sublimate on the upper part of the containing vessel was collected and proved to be stilbene (m.p. and mixed m.p.). The reddish sublimate on the lower part of the vessel was collected and proved to be the quinone (m.p. and mixed m.p.).

*Photoreaction of the quinone* I *with benzalphthalide.* The quinone (0.7 g.) and benzalphthalide (1.0 g.) in benzene (45 ml.) was irradiated for 7 days (March). The photoproduct VII separated during irradiation as colorless crystals. It was recrystallized from chlorobenzene, m.p. 333°. Yield, ca., 78%.

*Anal.* Calcd. for $C_{31}H_{19}N_3O_4$: N, 8.45. Found: N, 8.28.

VII is insoluble in aqueous sodium hydroxide solution and develops no color with ferric chloride.

*Photoreaction of 2-N-phenyl-α,β-naphtho-1,2,3-triazolquinone monoxime* (IV) *and p-methoxybenzaldehyde.* A mixture of the oxime (IV) (0.8 g.) and *p*-methoxybenzaldehyde (0.9 g.) in benzene (80 ml.) was exposed to sunlight for 28 days (March). A colorless photoproduct separated during irradiation. It was recrystallized from xylene as almost colorless crystals, m.p. 250–251°. Yield ca., 48%.

*Anal.* Calcd. for $C_{24}H_{18}N_4O_4$: N, 13.14. Found: N, 12.70.

The product is insoluble in cold aqueous sodium hydroxide solution; it gives a yellow color with concd. sulfuric acid and develops no color with ferric chloride.

This photoproduct was heated at 255° (bath temperature) under reduced pressure (oil-pump) for 0.5 hr. The containing vessel was then cooled and the substance obtained after heating was identified as Va.

*Action of p-methoxybenzaldehyde on the monoxime* IV *in the dark.* A mixture of the monoxime (IV) (0.3 g.), anisaldehyde (0.4 g.) and a few drops of piperidene was heated at 160–170° (bath temperature) for 2 hr. The reaction mixture was then cooled, rubbed with benzene, filtered on the pump, and washed with cold benzene. The product was recrystallized from xylene as colorless crystals, m.p. 275°. Yield, ca., 71%.

*Anal.* Calcd. for $C_{24}H_{16}N_4O_2$: C, 73.46; H, 4.08; N, 14.28. Found: C, 73.68; H, 4.00; N, 14.41.

Va is insoluble in aqueous sodium hydroxide solution; it gives a yellow color with concd. sulfuric acid and developed no color with ferric chloride.

*Action of 3,4-diethoxybenzaldehyde on the monoxime in the dark.* A mixture of the monoxime (0.5 g.), 3,4-diethoxybenzaldehyde (0.6 g.), and 2 drops of piperidene was heated at 165–170° (bath temperature) for 2 hr. It was then cooled and the dark residue obtained washed with cold ethanol. Recrystallization from acetic acid gave almost colorless crystals m.p. 219°. Yield, ca., 41%.

*Anal.* Calcd. for $C_{27}H_{22}N_4O_3$: N, 12.44. Found: N, 12.03.

Vb is insoluble in aqueous sodium hydroxide solution and develops no color with ferric chloride.

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(7a) The photoreactions were carried out in Schlenk tubes of pyrex glass [W. Schlenk and A. Thal, *Ber.*, **46**, 2840 (1913)]. The benzene used for the photochemical experiments was thiophen-free and dried over metallic sodium. Parallel experiments were carried out in the dark under the same experimental conditions and proved to be negative.