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MESOIONIC 1-PHENYLIMINO-2,4,5-TRIPHENYL-1,2,3-TRIAZOLE : A NEW 1,3-DIPOLAR SYSTEM

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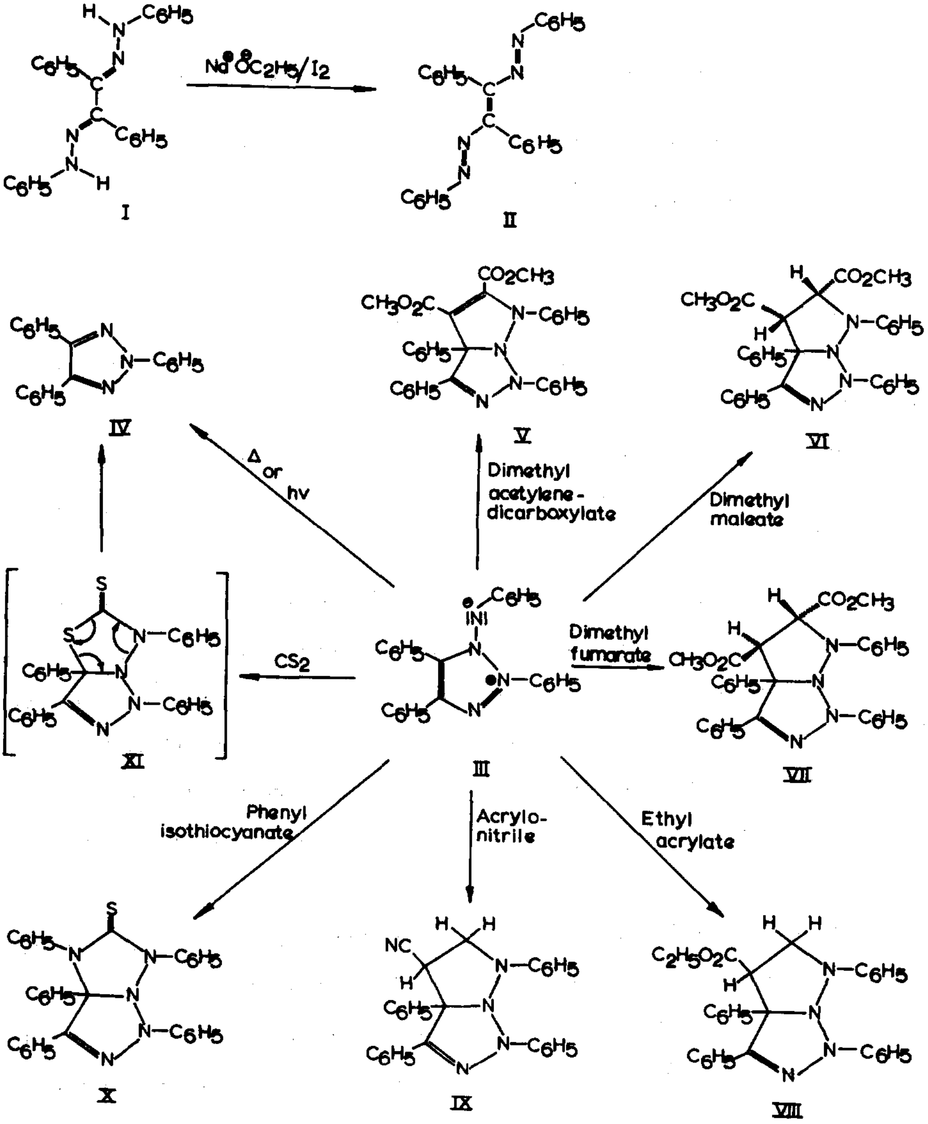
The structures of the oxidation products of bis-phenylhydrazones and bis-benzoylhydrazones of 1,2-diketones have been investigated by several group of workers. Pechmann[2] had reported that the intensely coloured products formed from the oxidation of bis-phenylhydrazones of 1,2-diketones were dihydro-1,2,3,4-tetrazine derivatives. Subsequent studies have shown that these compounds were in fact bis-azoolefins.[3] This view was supported by spectroscopic evidences[4] and by studies on liquid crystals.[5]

In a detailed investigation, Curtin and Alexandrou[6] have shown that the colourless solids obtained from the oxidation of bis-benzoylhydrazones of 1,2-diketones were enol benzoates and not the dihydro-1,2,3,4-tetrazine derivatives, as formulated by earlier workers.[3,7] These enol benzoates have been shown to undergo ready rearrangement to dibenzoylamino derivatives.[6,8] It might be mentioned in this connection that Katritzky and coworkers have observed that certain ortho bisazo compounds containing electron withdrawing groups attached to one of the azo groups exist in the mesoionic form.[9,10]

It has been reported by Spasov and coworkers[11] that benzil osazone (I) exists in different isomeric forms and that the product formed on oxidation with sodium ethoxide and iodine is bis-phenylazostilbene (II).[12] In the present investigation, we have examined some of the reactions of the oxidation product of benzil osazone and feel that these reactions can be rationalized only through the mesoionic intermediate III.

Heating II in the absence of any solvent for fifteen minutes around 170° results in the formation of a 85% yield of 2,4,5-triphenyl-1,2,3-triazole (IV). The same triazole was obtained in a 14% yield, on photolysis of II in benzene.[13] The formation of the triazole IV may be explained in terms of the loss of phenylnitrene from the mesoionic intermediate III. It is probable that III exists in equilibrium with II, under our reaction conditions.

SCHEME 1


I
II
Na⊕ ⊖OC2H5/I2
III
IV
V
VI
VII
VIII
IX
X
XI
Δ or hν
Dimethyl acetylenedicarboxylate
Dimethyl maleate
Dimethyl fumarate
CS2
Phenyl isothiocyanate
Acrylonitrile
Ethyl acrylate
C6H5
CO2CH3
CH3O2C
C2H5O2C
NC

The mesoionic, 1-phenylimino-2,4,5-triphenyl-1,2,3-triazole (III) represents a 1,3-dipolar system and in tune with our expectations, we find that III undergoes cycloaddition reactions with different dipolarophiles. Treatment of III with dimethyl acetylenedicarboxylate in refluxing acetone gives a 83% yield of the adduct V, m.p. 184°. Similarly, the reaction of III with dimethyl maleate, dimethyl fumarate, ethyl acrylate, acrylonitrile and phenylisothiocyanate gave the corresponding adducts, VI, m.p. 200° (79%), VII, m.p. 205° (74%), VIII, m.p. 216° (76%), IX, m.p. 249° (81%) and X, m.p. 268° (60%) (Scheme 1).

The reaction of III with carbon disulphide resulted in the formation of a 85% yield of the triazole IV and a 51% yield of phenylisothiocyanate. The formation of these products can be explained through the intermediate XI, which undergoes fragmentation with the loss of sulphur.

The structures of all the new products have been arrived at on the basis of analytical results and spectral evidences.

A detailed investigation on the structure and reactions of similar mesoionic systems is currently under progress.

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13) On completion of our work we came across a brief communication dealing with the photolysis of III [C. Wintner, *Tetrahedron Letters*, 2275 (1970)], which prompted us to publish some of our experimental findings.