Photolyses of Some Mesoionic Ring Systems

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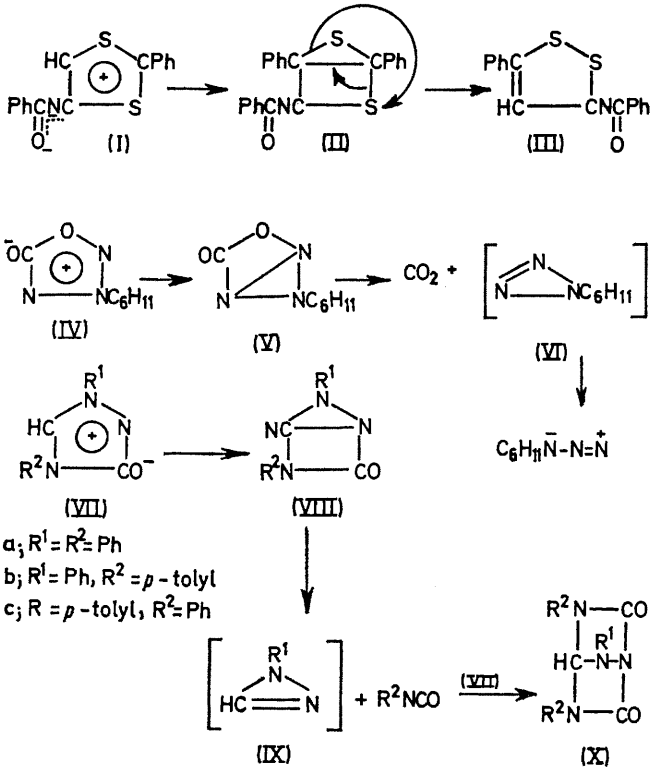
Summary Photo-electrocyclic valence isomerisation to bicyclic systems are suggested as the initial stage of the photolyses of the mesoionic dithiolimine (I), oxatriazolone (IV), and triazolone (VII).

As part of our studies on the photochemical behaviour of mesoionic compounds,[1] we briefly surveyed photolyses of other mesoionic ring systems.

The irradiation through Pyrex of a benzene solution of mesoionic *N*-benzoyl-2-phenyl-1,3-dithiol-4-imine (I)[2] gave an 80% yield of *N*-benzoyl-5-phenyl-1,2-dithiol-3-imine (III).[3] The photolysis of mesoionic 3-cyclohexyl-1,2,3,4-oxatriazol-5-one (IV)[4] under the same conditions afforded cyclohexanone in 27% yield, accompanied by a trace amount of cyclohexylamine.

The irradiation through Pyrex of a solution of mesoionic 1,4-diphenyl-1,2,4-triazol-3-one (VIIIa)[5] in methylene chloride resulted in the formation of phenyl isocyanate (13% yield), diphenylurea (23% yield), and a phenyl isocyanate adduct of (VIIa) (49% yield). The adduct had only one carbonyl absorption band at 1745 cm^{-1} and was decomposed to phenyl isocyanate and (VIIa) on heating, and hence, a symmetrical bicyclic structure (X; $R^1 = R^2 = \text{Ph}$) was assigned to this adduct. The photolytic behaviour of this ring system is influenced by the substituents on the ring. Thus, the irradiation of the 1-phenyl-4-*p*-tolyl derivative (VIIb) gave *p*-tolyl isocyanate (38% yield), a trace of phenyl isocyanate, and di-*p*-tolylurea (1·3% yield). The photolysis of the 4-phenyl-1-*p*-tolyl derivative (VIIc) afforded phenyl isocyanate (13% yield), *p*-tolyl isocyanate (0·1% yield), diphenylurea (1·7% yield), and a fourth product identified as 1-formyl-4-phenyl-1-*p*-tolylsemicarbazide (26% yield). In neither case was the isocyanate adduct corresponding to (X) isolated.



These findings support our earlier suggestion that the first stage in the photochemical transformation of many mesoionic ring systems is an electrocyclic reaction to bicyclic rings.[1] Thus, a photo-disrotatory ring closure of (I), which is both sterically and symmetry allowed,[6] gives a bicyclic intermediate (II), which, instead of giving fragmentation products, undergoes a 1,3-sigmatropic rearrangement to give (III). Similarly, oxatriazolone (IV) is first converted into a bicyclic lactone (V), which decomposes to carbon dioxide and (probably *via* anti-aromatic 3-cyclohexyltriazirine) cyclohexyl azide, which ultimately affords cyclohexanone by photolysis followed by hydrolysis.[6] Lastly, mesoionic triazolone (VII) is first converted in an analogous fashion into a bicyclic intermediate (VIII), which then yields isocyanate, and under suitable circumstances, the isocyanate adds photolytically to either (VII) or (VIII) to give cycloadduct (X). [Isocyanate does not add to (VII) in the dark.] Attempts at trapping the possible remaining intermediate, an anti-aromatic 1-aryl-2-diazirine (IX) or its open-chain isomers, have so far been unsuccessful. Although the fate of this remaining moiety is not yet known, experiment shows that a small fraction of it was rearranged to carbodi-imide, which was hydrolysed to isocyanate. No *N*-phenylcyanamide was detected in the photolysate of (VIIa).

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