

A Photo-oxide of the 1,2' Dimer of the 2,4,5-Triphenylimidazolyl (Lophyl) Radical

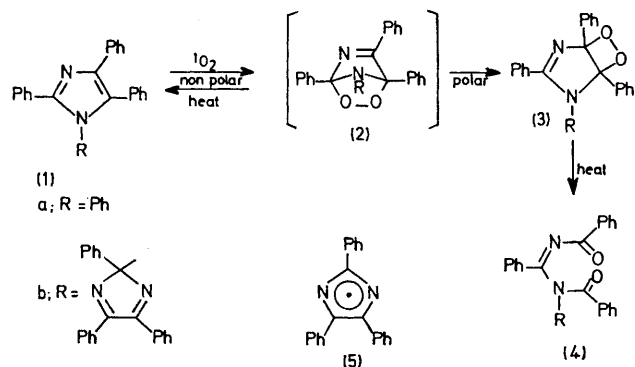
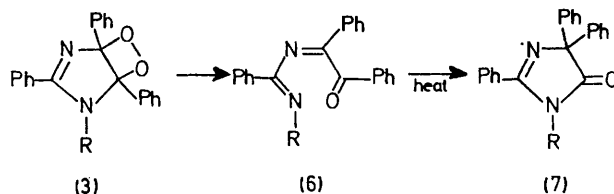
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Summary The 4,5-epidioxide of 2,4,5-triphenyl-1-(2,4,5-triphenyl-2*H*-imidazol-2-yl)imidazole is obtained by methylene blue sensitised photo-oxidation at -50°C ; it undergoes isomerisation, reduction, and degradation reactions, leading *inter alia* to 2-benzoyl-1,2-dihydro-2,4,6-triphenyl-1,3,5-triazine and 1,3a,4(6),6a-tetrahydro-2,3a,5,6a-tetraphenylimidazo[4,5-*d*]imidazole.

product was the diacylamidine (**4a**), which resulted from cleavage of the hypothetical 4,5-epidioxide (dioxetan) (**3a**), the latter arising from solvent-induced isomerisation of (**2a**). Recently, the imidazolinone (**7a**) has been obtained by photo-oxidation in the presence of diphenyl sulphide, which is a reducing agent of the dioxetan (**3a**).⁴ We now

2,4,5-TRIARYLIMIDAZOLES, *e.g.* lophine, readily form 4-hydroperoxy derivatives by sensitised photo-oxidation,¹ but no peroxides seem to have been isolated so far from 1,2,4,5-tetrasubstituted imidazoles. However, direct evidence for



the existence of such a peroxide, *e.g.* the 2,5-epidioxide (**2a**), in a weakly polar solvent (ether) at -60°C , has been given.² In polar solvents (CHCl_3 ,² MeOH ³) the only

report isolation of the dioxetan (**3b**), derived from the 1,2' dimer (the photochromic dimer) (**1b**),⁵ of the 2,4,5-triphenylimidazolyl (lophyl) radical, (**5**). Isolation is more likely for (**3b**) because of the size of the molecule.

Photo-oxidation (1.5 h) of (**1b**) in polar solvents [*ca.* 1.7×10^{-3} M, CH_2Cl_2 - MeOH or CHCl_3 - MeOH , -50°C (dissociation to (**5**) negligible), methylene blue, oxygen stream, chromate filter, tungsten lamps⁶] yields the pale yellow dioxetan (**3b**), m.p. 117°C (decomp.)[†] (70%). It slowly isomerises at 20°C in solution or (quantitatively) in the solid state to the diacylamidine (**4b**), m.p. 128 – 130°C (decomp.). An intermediate pink colour is attributed to the radical (**5**) on the basis of visible and e.s.r. spectra. This implies that isomerisation involves, at least in part, 1,2' bond cleavage and recombination. Cleavage is prob-

[†] Satisfactory analytical and spectroscopic data have been obtained for all new compounds.

ably induced by dioxetan ring opening, since (4b) is stable under these conditions.

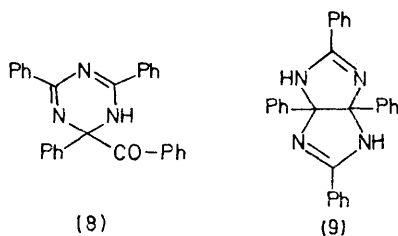


Photo-oxidation in a weakly polar solvent (CS_2 , -50°C , methylene blue adsorbed on alumina⁷), followed by addition of CH_2Cl_2 -MeOH at -50°C , gives rise to the diacylamidine (4b) (66%) in addition to the dimer (1b) (16%). Recovery of the latter is greater (44%) in the absence of CH_2Cl_2 -MeOH [(4b), 49%]. Thus, the intermediacy of the 2,5-epidioxide (2b) in all photo-oxidation conditions seems highly probable.

Reduction of (3b) with triphenylphosphine in neutral solution (ether, -20°C) produces the acylalkylideneamidine (6b), m.p. 174 – 175°C (66%), which on heating readily

isomerises to the imidazolinone (7b), m.p. 187 – 189°C (96%). In acid solution (PPh_3 , MeOH, *p*-toluenesulphonic acid, -50°C), (3b) undergoes complete deoxygenation to (1b) (76%).

Reduction of (3b) with sodium iodide at -50°C affords as major products benzil, the pale yellow acyldihydrotriazine (8), m.p. 193 – 194°C , and the bicyclic diamidine (9), m.p. 378 – 380°C ; minor products are (4b), 2,4,6-triphenyltriazine and lophine. The predominant product is (8) in neutral solution (MeOH), and (9) under acidic conditions (MeOH-AcOH). The same compounds are formed in the alkaline hydrolysis of (4b) and in the hydrolysis on silica gel of (6b).

Proofs of the structure of compounds (8) and (9) and discussion of the reaction mechanisms will be given in the full paper.

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