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

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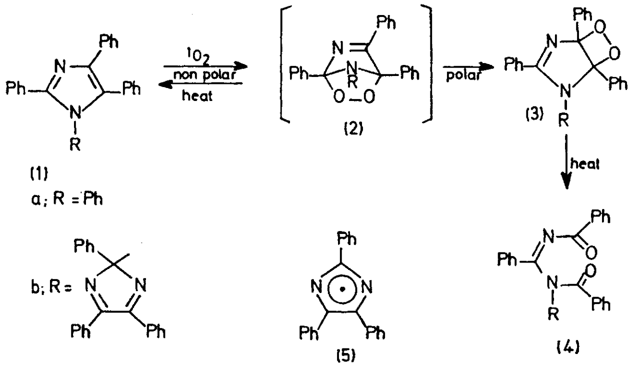
Summary The 4,5-epidioxide of 2,4,5-triphenyl-1-(2,4,5-triphenyl-2*H*-imidazol-2-yl)imidazole is obtained by methylene blue sensitised photo-oxidation at −50 °C; it undergoes isomerisation, reduction, and degradation reactions, leading *inter alia* to 2-benzoyl-1,2-dihydro-2,4,6-triphenyl-1,3,5-triazine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

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 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 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.



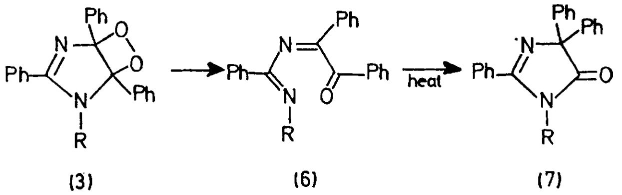


Photo-oxidation (1·5 h) of (**1b**) in polar solvents [*ca.* 1·7 × 10^{-3} M, CH_2Cl_2–MeOH or $CHCl_3$–MeOH, −50 °C (dissociation to (**5**) negligible), methylene blue, oxygen stream, chromate filter, tungsten lamps[6]] yields the pale yellow dioxetan (**3b**), m.p. 117 °C (decomp.)† (70%). It slowly 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-

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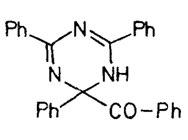
† Satisfactory analytical and spectroscopic data have been obtained for all new compounds.

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



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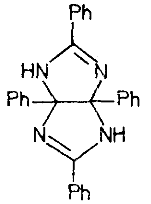

(9)

Photo-oxidation in a weakly polar solvent (CS_2, −50 °C, methylene blue adsorbed on alumina[7]), 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.

We thank Mrs. M. Masure for first attempts to isolate (**3b**), Professor J. Livage (E.N.S.C., Paris) for a preliminary e.s.r. spectrum of (**5**), Dr. J. Roncin (Université de Paris-Sud) for its complete identification, and the Centre de recherches Roussel-UCLAF for microanalyses.

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