A New Photo-oxidation: The Transformation of Lactams into Imides

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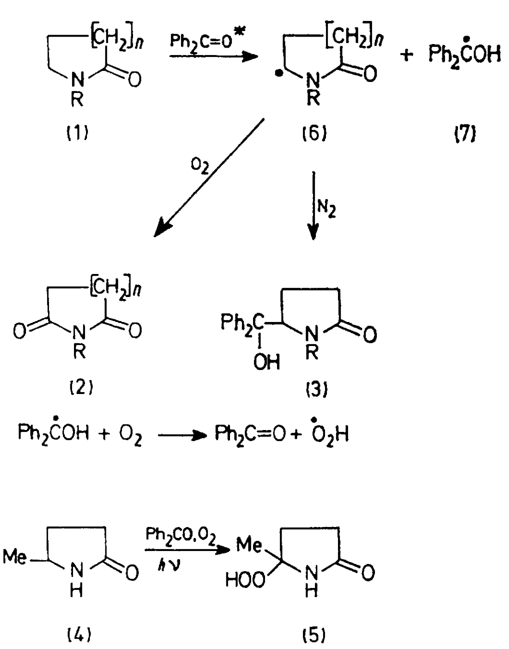
Summary Lactams are photochemically oxidized in solution by benzophenone and molecular oxygen to the corresponding imides or hydroperoxides.

Chemical oxidations of lactams are typically complex and lead to a wide variety of products.[1] At present, only one general method is available for the oxidation of lactams to imides, which is based on the use of peroxides, and is slow in some cases, and involves acidic conditions in others. We have sought an alternative method and report now a new reaction which converts lactams into imides smoothly under neutral conditions without the use of peroxides.†



SCHEME

Irradiation (medium-pressure Hanau mercury vapour lamp, 150 W, Pyrex reactor) of an oxygen-saturated solution in Bu^{t}OH (70 ml) of *N*-methylpyrrolidone (**1**; R = Me, $n = 1$) (2 g) and benzophenone (1 g) saturated with O_2 yielded *N*-methylsuccinimide (**2**; R = Me, $n = 1$) in 60% isolated yield (column chromatography on silica gel). Under the same conditions, pyrrolidone (**1**; R = H, $n = 1$) and *N*-methylpiperidone (**1**; R = Me, $n = 2$) are converted with equal efficiency into succinimide (**1**; R = H, $n = 1$) and *N*-methylglutarimide (**2**; R = Me, $n = 2$), respectively. In all cases the products were stable under the reaction conditions and were identified by comparison with an authentic sample.

Presumably, oxidation is initiated by abstraction of the hydrogen α to the amide carbonyl by triplet benzophenone in the usual way.[3] Subsequent steps are then straightforward (Scheme). This rationalization is supported by several additional considerations: (a) no reaction occurs in the absence of benzophenone; (b) reaction under nitrogen leads to formation of the adduct (**3**; R = Me), m.p. 215—216 °C, from combination of radicals (**6**; R = Me, $n = 1$) and $Ph_2\dot{C}OH$; and (c) 5-methylpyrrolidone (**4**) yields the hydroperoxide (**5**), m.p. 155—162 °C (decomp.), presumably *via* the radical (**6**; R = Me, $n = 1$).

The present reaction contrasts with the previously reported photoalkylation of pyrrolidone[4] (using acetone as sensitizer) and photo-oxidation of other lactams[5] (using sodium anthraquinone-2,6-disulphonate as sensitizer) by virtue of the site specific formation of the intermediate radical α to nitrogen only.

Intervention of singlet oxygen may be excluded since *N*-methylpyrrolidone is inert to it under all the usual conditions (visible light, oxygen, and eosin or Rose Bengal in Bu^{t}OH; u.v. light, oxygen, and naphthalene or triphenylene in benzene; and hydrogen peroxide and sodium hypochlorite in methanol[6]).

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† Satisfactory C, H, and N analyses and i.r., n.m.r., and mass spectra were obtained for new compounds.

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