Intramolecular Olefin Epoxidation observed in the Air Oxidation of 1-Phenyl-1-diazopent-4-ene Derivatives

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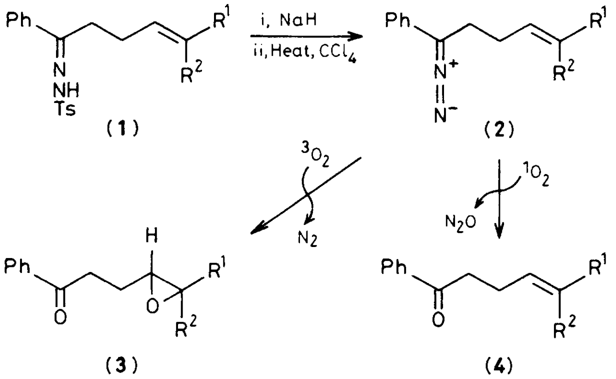
The simple air oxidation of 1-phenyl-1-diazopent-4-ene derivatives (**2**) under basic conditions (NaH) was found to involve an efficient intramolecular epoxidation to give epoxyketone (**3**), while the dye-sensitised photo-oxygenation reaction of (**2**) afforded ketone (**4**) exclusively.

It has been reported that the reaction of diazoalkanes with singlet oxygen generates carbonyl oxide,[1] which, in turn, intermolecularly transfers an oxygen atom to an olefin to give an epoxide.[2] The efficiencies of intermolecular oxygen atom transfer in this method are, however, reported to be low.[3] These results prompted us to study intramolecular oxygen atom transfer using diazoalkenes (**2**) which were generated to test the possibility of the intramolecular 1,1-cycloaddition reaction.[4] We report here that facile epoxidations occurred in the reaction of (**2**) with triplet molecular oxygen rather than with singlet oxygen.

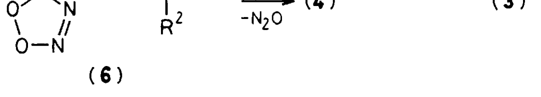
Upon decomposition of the sodium salt of (**1a**) in refluxing CCl_4, the solution immediately developed a red colouration owing to the generation of (**2a**) (i.r., 2025 cm^{-1} in CCl_4)[5] as sodium toluene-*p*-sulphinate was liberated. Compound (**2a**) was found to be stable and inert towards intramolecular cycloaddition and carbene formation even under reflux (CCl_4, N_2 atmosphere). When a solution of (**2a**) in CCl_4 containing sodium toluene-*p*-sulphinate and excess of NaH was exposed to air, with stirring at room temperature, however, the colour of the solution faded rapidly owing to the disappearance of (**2a**), and upon prolonged stirring the epoxyketone (**3a**) (m.p. 37 °C)† and the ketone (**4a**) (m.p. 56.5 °C) were isolated in 49 and 27% yields, respectively. Similarly, under the same conditions, (**2b**) (i.r., 2040 cm^{-1} in CCl_4) afforded 71% of (**3b**) (m.p. 51 °C)† and 14% of (**4b**) (m.p. 51 °C), and (**3c**) (m.p. 30 °C)† and (**4c**) were isolated from (**2c**) (i.r., 2035 cm^{-1} in CCl_4) in 25 and 28% yields, respectively (Scheme 1).



a; $R^1 = Ph, R^2 = H$
b; $R^1 = R^2 = Ph$
c; $R^1 = R^2 = H$

Scheme 1. Ts = *p*-$MeC_6H_4SO_2$.

It is of interest that the air oxidation of (**2a**) under neutral conditions‡ and dye-sensitised photo-oxidations of (**2a**) using *meso*-tetraphenylporphine (both under the basic and neutral conditions) afforded the ketone (**4a**) exclusively. The fact that the air oxidation of (**2a**) in the presence of the ketone (**4b**) under the basic conditions did not afford (**3b**) excludes a simple air epoxidation path from (**4**) to (**3**), but suggests an



Scheme 2

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† ^1H N.m.r. data for (**3a**)—(**3c**) δ (CCl_4), (**3a**): 1.90 (m, 1H), 2.25 (m, 1H), 2.90 (m, 1H), 3.10 (t, *J* 7.5 Hz, 2H), 3.54 (d, *J* 2.2 Hz, 1H), 6.90—7.50 (m, 8H), and 7.80—8.00 (m, 2H); (**3b**): 1.50 (m, 1H), 1.96 (m, 1H), 3.02 (t, *J* 7.5 Hz, 2H), 3.40 (dd, *J* 7.5, 4.5 Hz, 1H), 7.05—7.55 (m, 13H), and 7.70—7.93 (m, 2H); (**3c**): 1.70 (m, 1H), 2.10 (m, 1H), 2.38 (dd, *J* 5.2, 5.1 Hz, 1H), 2.61 (dd, *J* 5.2, 4.0 Hz, 1H), 2.90 (m, 1H), 3.05 (t, *J* 7.0 Hz, 2H), 7.20—7.60 (m, 3H), and 7.80—8.05 (m, 2H).

‡ After decomposition, the red CCl_4 solution was neutralised by washing with water to remove sodium toluene-*p*-sulphinate and excess of NaH and then dried over Na_2SO_4 under N_2.

internal oxygen atom transfer possibly *via* carbonyl oxide. In fact, addition of dimethyl sulphide[6] changed the product ratio, (**3a**) : (**4a**), from 62:38 to 15:85. These observations do not contradict the previous observation that carbonyl oxide is generated from diazoalkane with singlet oxygen if we assume that carbonyl oxide can be generated from diazomethane, not only with singlet oxygen but also with triplet oxygen, and the efficiency of oxygen atom transfer mainly depends on that of the formation of carbonyl oxide from an initially formed diazomethane-oxygenated species.

A plausible mechanism for the intramolecular epoxidation is shown in Scheme 2. The reaction of (**2**) with triplet oxygen initially forms the zwitterionic species (**5**) much faster under the basic conditions than under the neutral conditions,§ whereas singlet oxygen exclusively forms the 1,3-dipolar cycloadduct (**6**) as suggested by Bethell and McKeivor[7] under both the basic and neutral conditions. Under the basic conditions the nitrogen extrusion reaction of (**5**) giving (**7**) occurs faster than the cyclisation to (**6**), while (**5**) cyclises to (**6**) with ease under the neutral conditions. Compound (**7**) then internally transfers an oxygen atom to the double bond to give (**3**). In contrast, (**6**) collapses to (**4**) releasing N_2O as the exclusive pathway.

Although toluene-*p*-sulphinate and the remaining NaH are assumed to stabilise the ionic state of (**5**) and accelerate the consumption of molecular oxygen by (**2**) under the basic conditions, their real effects are still ambiguous. Nevertheless, the results presented here provide the first example of oxygen atom transfer *via* carbonyl oxide generated from a diazoalkene with triplet molecular oxygen.

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§ Compound (**2a**) disappeared within 30 min under the basic conditions which is 66 times faster than the disappearance of (**2a**) under the neutral conditions.

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