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An Easy Construction of 8,12-Dioxa-13-azatricyclo[8.3.1.$0^{2,7}$]tetradeca-2(7),3,5,13-tetraen-14-ones

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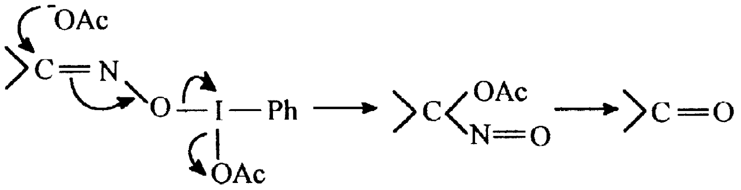
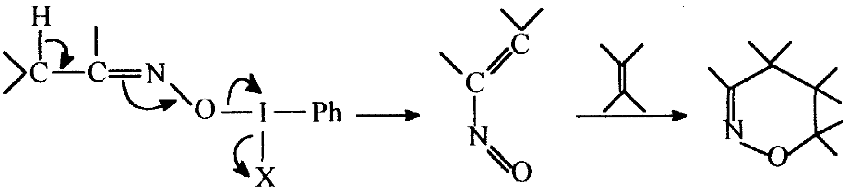
Abstract: 8,12-Dioxa-13-azatricyclo[8.3.1.$0^{2,7}$]tetradeca-2(7),3,5,13-tetraen-14-ones are obtained in moderate yield by treatment of oximes of *o*-allyloxyacetophenones with [hydroxy(tosyloxy)iodo]benzene in acetonitrile.

Deoximation of ketoximes utilising (diacetoxyiodo)benzene (DAIB)[1a,b] or (dichloroiodo)benzene (DCIB)[1c] is one of the many important synthetic applications of hypervalent iodine reagents reported in recent years.[2] The suggested mechanism for the reaction with DAIB[1a,b] is as follows :



We envisaged that if the reaction is done by using a hypervalent iodine reagent unable to supply nucleophile of sufficient nucleophilicity, then the 1,4-elimination reaction shown below would be a competitive process. The product of such reaction, a nitrosoalkene, can undergo [4+2]-cycloaddition[3] with a double bond (intramolecular or intermolecular), constituting a simple method for synthesis of interesting 5,6-dihydro-4H-1,2-oxazine derivatives. We report here the preliminary interesting results obtained from the reaction on oximes (**1**) of *o*-allyloxyacetophenones utilising [hydroxy(tosyloxy)iodo]benzene (HTIB) as the reagent.



On addition of HTIB to a solution of **1** in dry acetonitrile, the colour changed to bluish green, indicating the formation of nitroso compound. Therefore, solid HTIB (1 equiv.) was added in portions during 1 hr. to a solution of **1** in the said solvent and the mixture was stirred for further 6 hr. Usual work up of the reaction mixture[4] followed by chromatographic resolution of the product mixture gave 8,12-dioxa-13-azatricyclo[8.3.1.$0^{2,7}$]tetradeca-2(7),3,5,13-tetraen-14-ones (**2**)[5] as a new type of product (yield : 30-34%)

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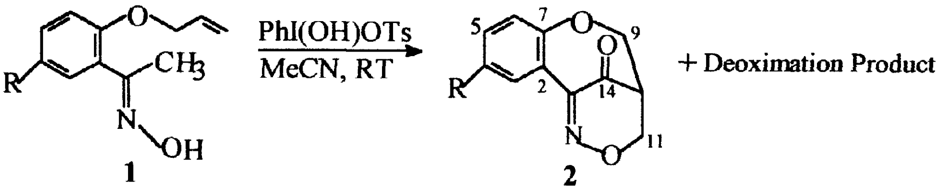
along with the deoximation product (22-26%).



a : R=H ; **b** : R=Me ; **c** : R=Cl

The compounds **2a-c** are obviously the product of the desired cycloaddition followed by an oxidation. The oxidation may be effected either by hypervalent iodine[6] or by aerial oxygen[7]. The interesting structural features of **2a-c** are that they contain a bridgehead double bond and a bridging >C=O. Another interesting aspect of such molecules is the possibility of their conversion to biologically important vicinal amino alcohols[8] through reduction.[3c]

Thus, we describe a new method for generation of nitrosoalkenes and their cycloaddition reaction in intramolecular fashion, which, to our knowledge, was not known previously. The most widely used method for generation of nitrosoalkenes involves a base-catalysed 1,4-elimination of hydrogen halide from the oximes of α-haloketones.[3] The present method appears to be a good substitute to that because it does not require the handling of lachrymatory and toxic α-haloketones. Furthermore, the observed regioselectivity in the cycloaddition process and the facile oxidation of the cycloaddition product are noteworthy.

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5. Selected data of **2** : **2a**, mp 93-94° (light yellow needles). Anal: Found C, 64.91; H, 4.30; N, 6.62, Calcd for $C_{11}H_9NO_3$ C, 65.02; H, 4.43; N,6.89%. IR (ν, KBr, cm^{-1}): 1650 (C=O), 1608 (C=N). ^1H NMR (300 MHz, $CDCl_3$) : δ 3.87-3.98 (1H, m, H-10), 4.24 (1H, dd, J= 11.7 and 7.4 Hz), 4.32 (1H, t, J=9.1 Hz), 4.39 (1H, dd, J= 11.7 and 5.5 Hz), 4.76 (1H, dd, J=11.1 and 8.9 Hz), 7.08 (1H, dd, J=8.2 and 0.9 Hz, H-6), 7.18 (1H, ddd, J=8.7, 7.9 and 0.9 Hz, H-4), 7.52 (1H, ddd, J=8.7, 8.2 and 1.7 Hz, H-5), 7.97 (1H, dd, J=7.9 and 1.7 Hz, H-3). ^{13}C NMR (75 MHz, $CDCl_3$) : δ47.30 (C-10), 71.86 (C-11), 74.80 (C-9), 122.57 (C-6), 124.05 (C-4), 127.90 (C-2), 130.77 (C-3), 135.91 (C-5), 158.18 (C-1), 159.52 (C-7), 182.41 (C-14). MS : M^+ 203. **2b**, mp 110-111°. **2c** mp 157-158°.
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